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Inventors : Roberto J. Rioja et al.
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Filed : October 3, 2003
For : ALUMINUM-COPPER-MAGNESIUM ALLOYS HAVING ANCILLARY ADDITIONS OF LITHIUM
Examiner : Janell Combs Morillo
Art Unit : 1742

DECLARATION OF ROBERTO J. RIOJA PURSUANT TO 37 C.F.R. § 1.132

List of Attachments

Attachment A	U.S. Application Serial No. 10/678,290 to Rioja et al.
Attachment B	Staley J. T., "Microstructure and Toughness of High Strength Aluminum Alloys," Properties Related to Fracture Toughness, ASTM STP 605, 1976, pp. 71-103.
Attachment C	U.S. Patent No. 5,455,003 to Pickens et al.

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(43) **Pub. Date: Apr. 15, 2004**

(54) ALUMINUM-COPPER-MAGNESIUM ALLOYS HAVING ANCILLARY ADDITIONS OF LITHIUM

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(22) Filed: **Oct. 3, 2003**

Related U.S. Application Data

(63) Continuation-in-part of application No. 09/104,123, filed on Jun. 24, 1998, now abandoned.

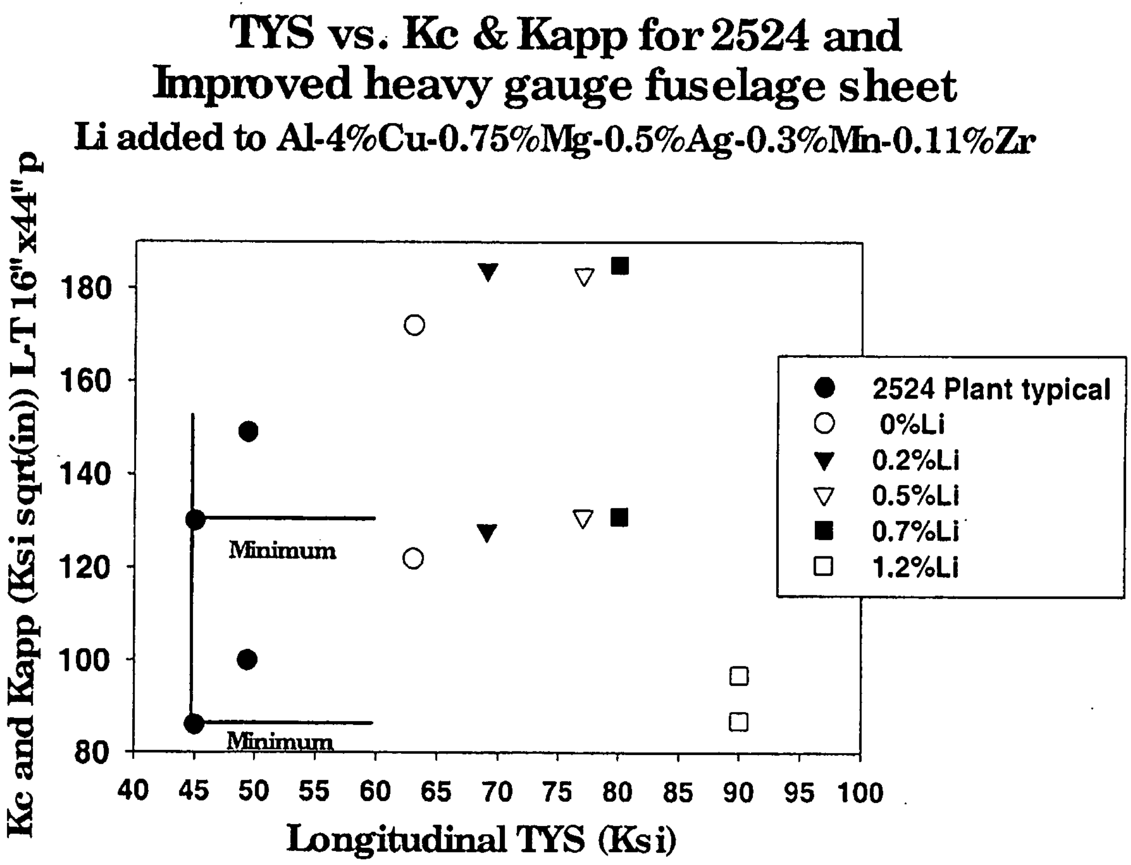
Publication Classification

(51) **Int. Cl.**^{7} **C22C 21/16**

(52) **U.S. Cl.** **420/532**; 420/533

(57) **ABSTRACT**

An aluminum-copper-magnesium alloy having ancillary additions of lithium. The alloy composition includes from about 3 to about 5 weight percent Cu, from about 0.5 to about 2 weight percent Mg, and from about 0.01 to about 0.9 weight percent Li. The combined amount of Cu and Mg is maintained below a solubility limit of the aluminum alloy. The alloys possess improved combinations of fracture toughness and strength, and also exhibit good fatigue crack growth resistance.



Composition Space Covering Al-Cu-Mg Alloys
With Ancillary Li Additions

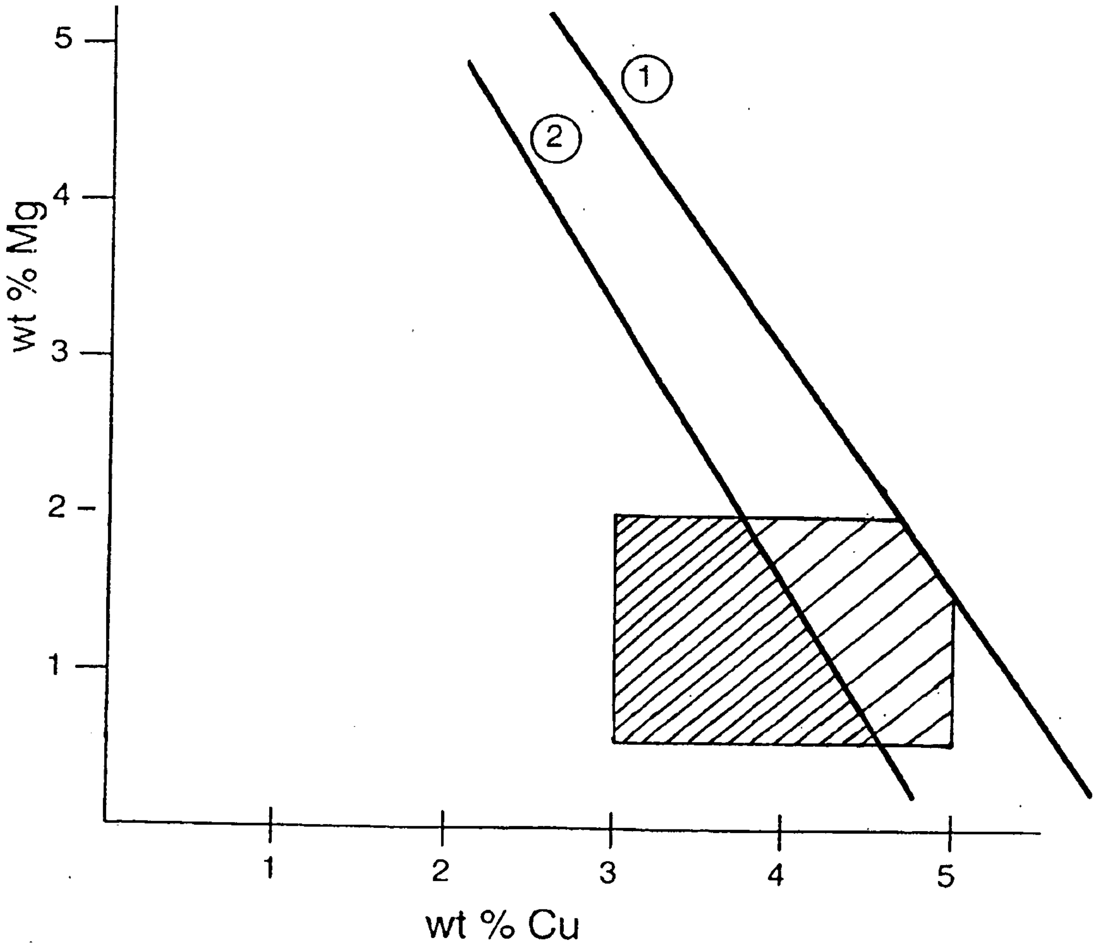


FIG. 1

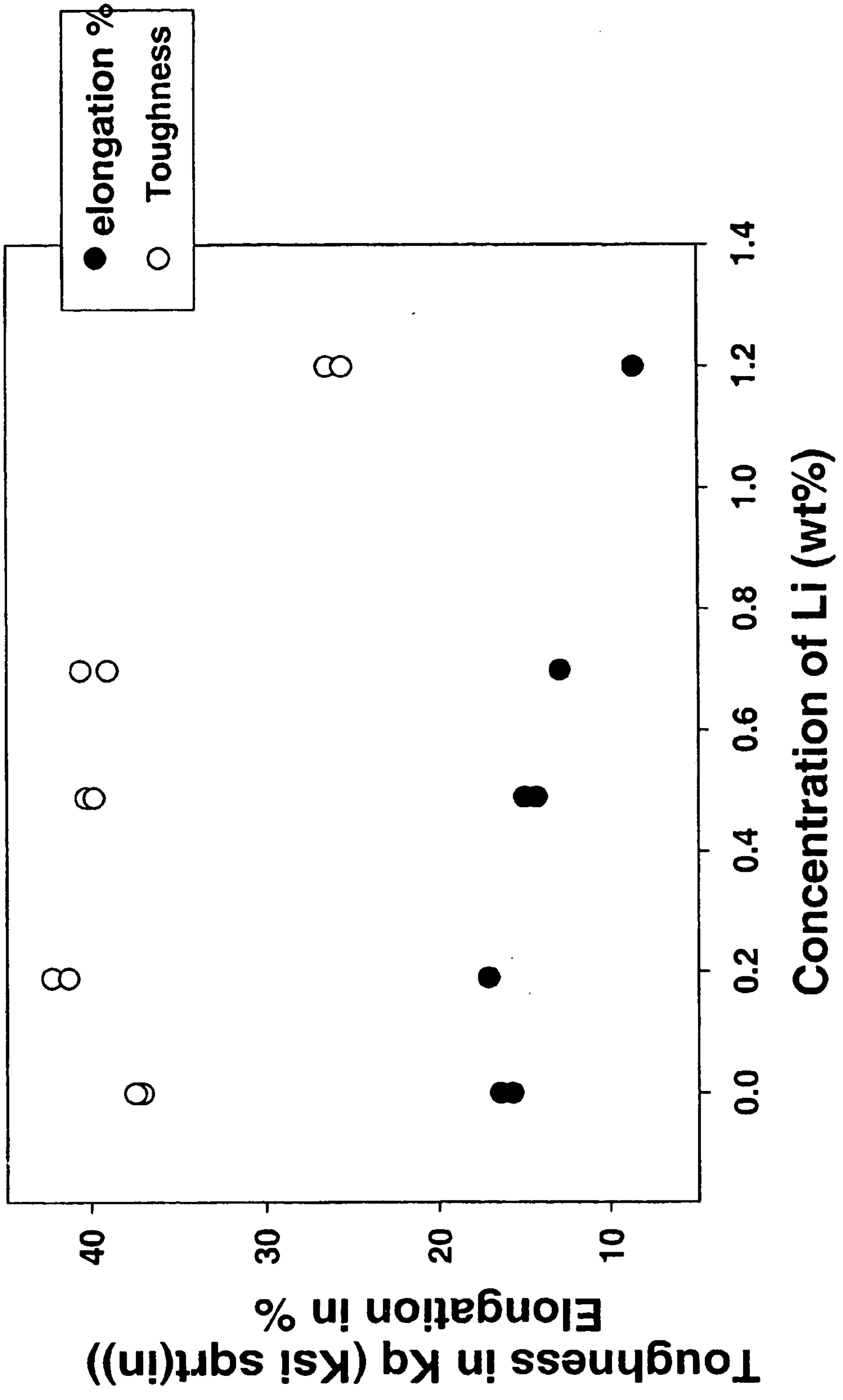

● elongation %
○ Toughness
Concentration of Li (wt%)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Toughness in Kq (Ksi sqrt(in))
Elongation in %
10
20
30
40

FIG. 2

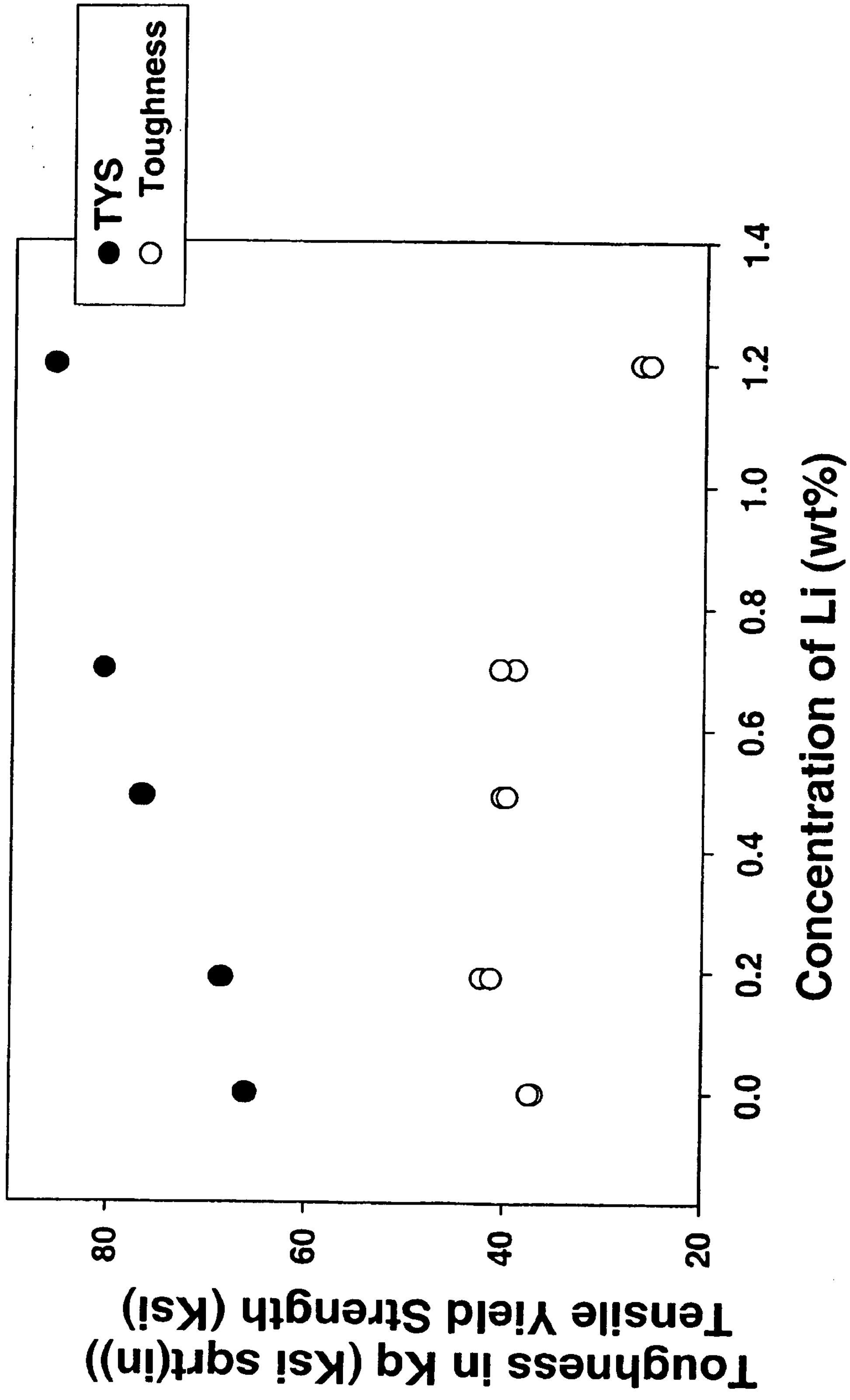

● TYS
○ Toughness
Tensile Yield Strength (Ksi)
Toughness in Kq (Ksi sqrt(in))
20
40
60
80
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Concentration of Li (wt%)

FIG. 3

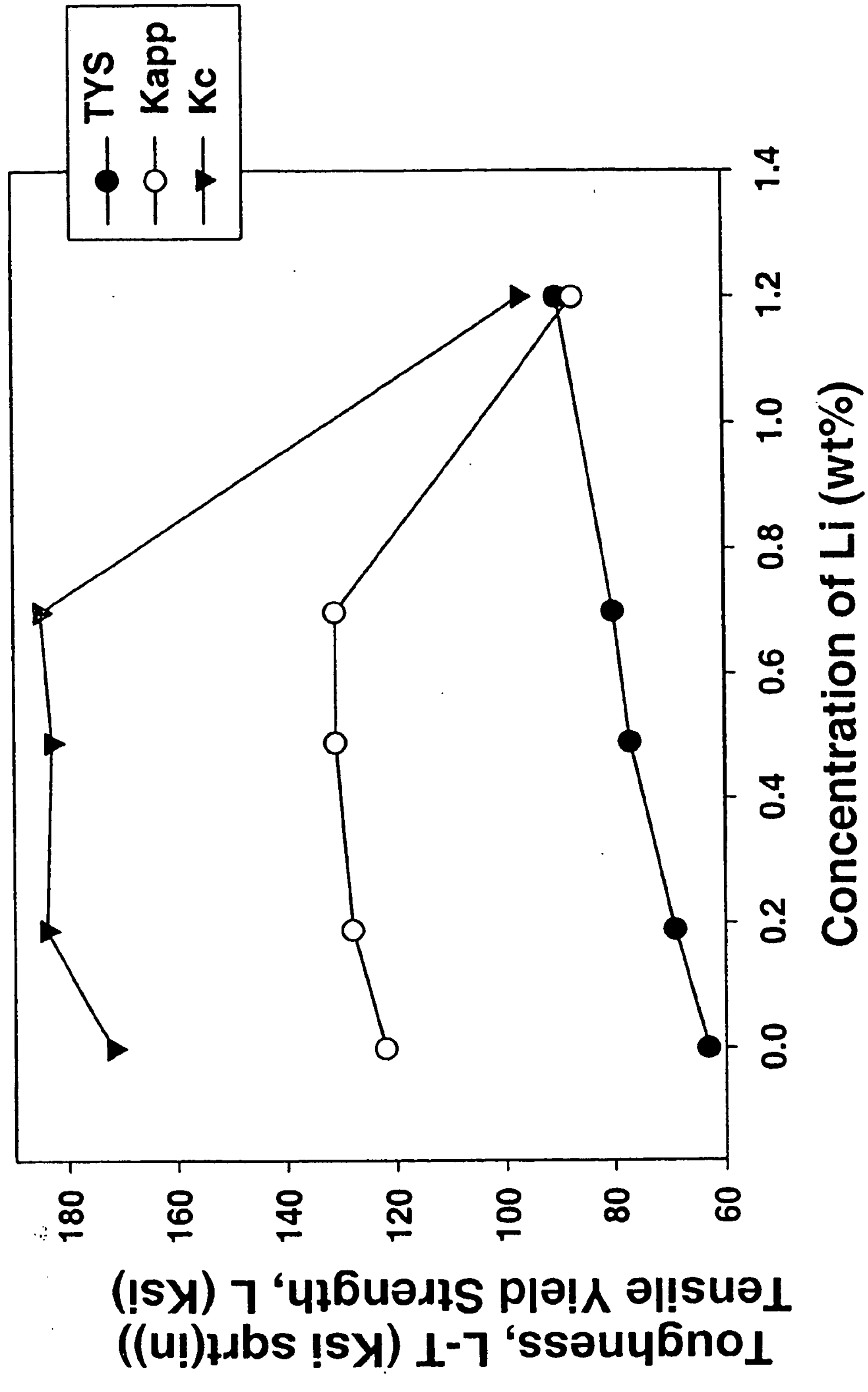

TYS
Kapp
Kc
Toughness, L-T (Ksi sqrt(in))
Tensile Yield Strength, L (Ksi)
180
160
140
120
100
80
60
Concentration of Li (wt%)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

FIG. 4

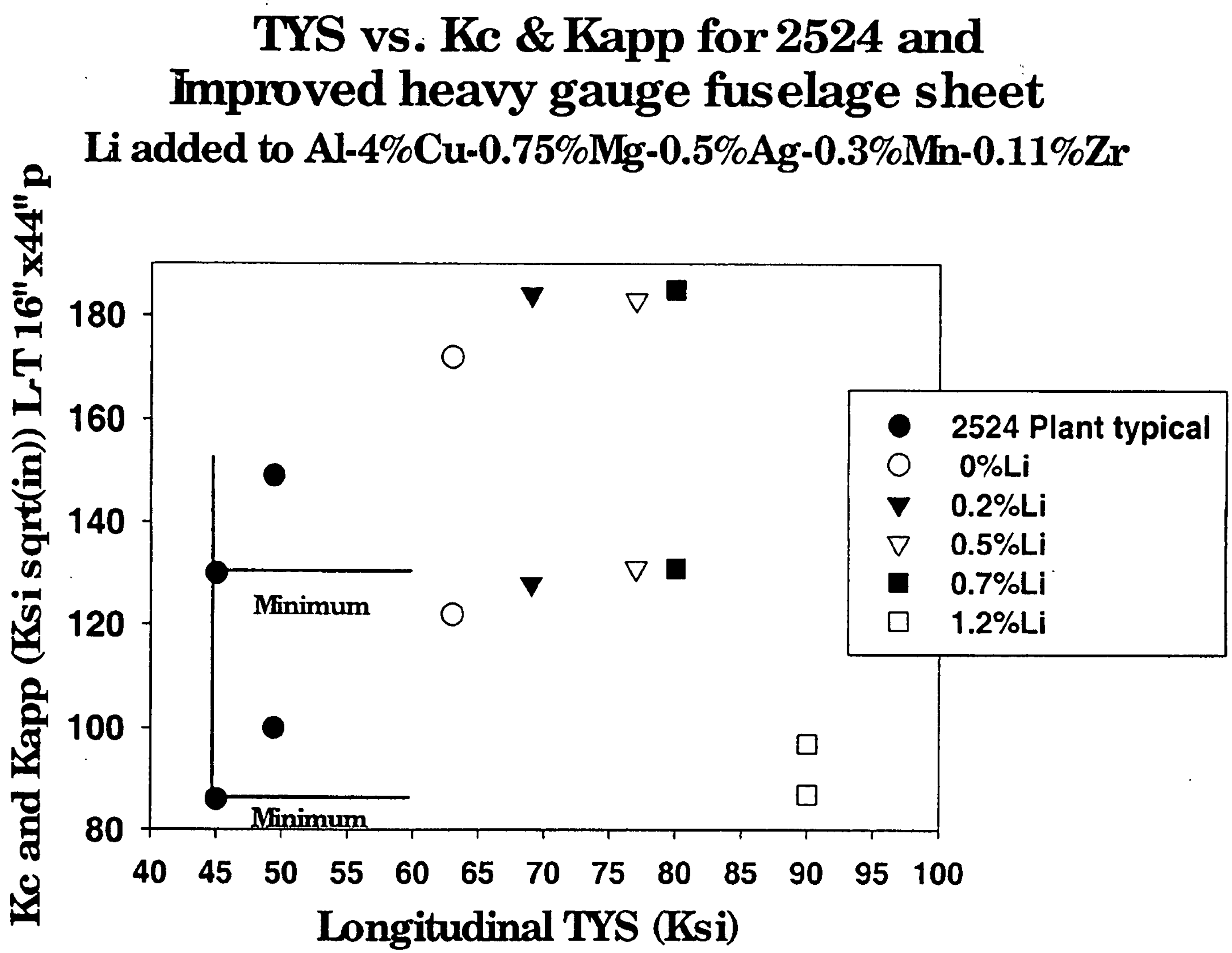

TYS vs. Kc & Kapp for 2524 and Improved heavy gauge fuselage sheet
Li added to Al-4%Cu-0.75%Mg-0.5%Ag-0.3%Mn-0.11%Zr
Kc and Kapp (Ksi sqrt(in)) L-T 16"x44"p
180
160
140
120
100
80
40
45
50
55
60
65
70
75
80
85
90
95
100
Longitudinal TYS (Ksi)
Minimum
Minimum
● 2524 Plant typical
○ 0%Li
▼ 0.2%Li
▽ 0.5%Li
■ 0.7%Li
□ 1.2%Li

FIG. 5

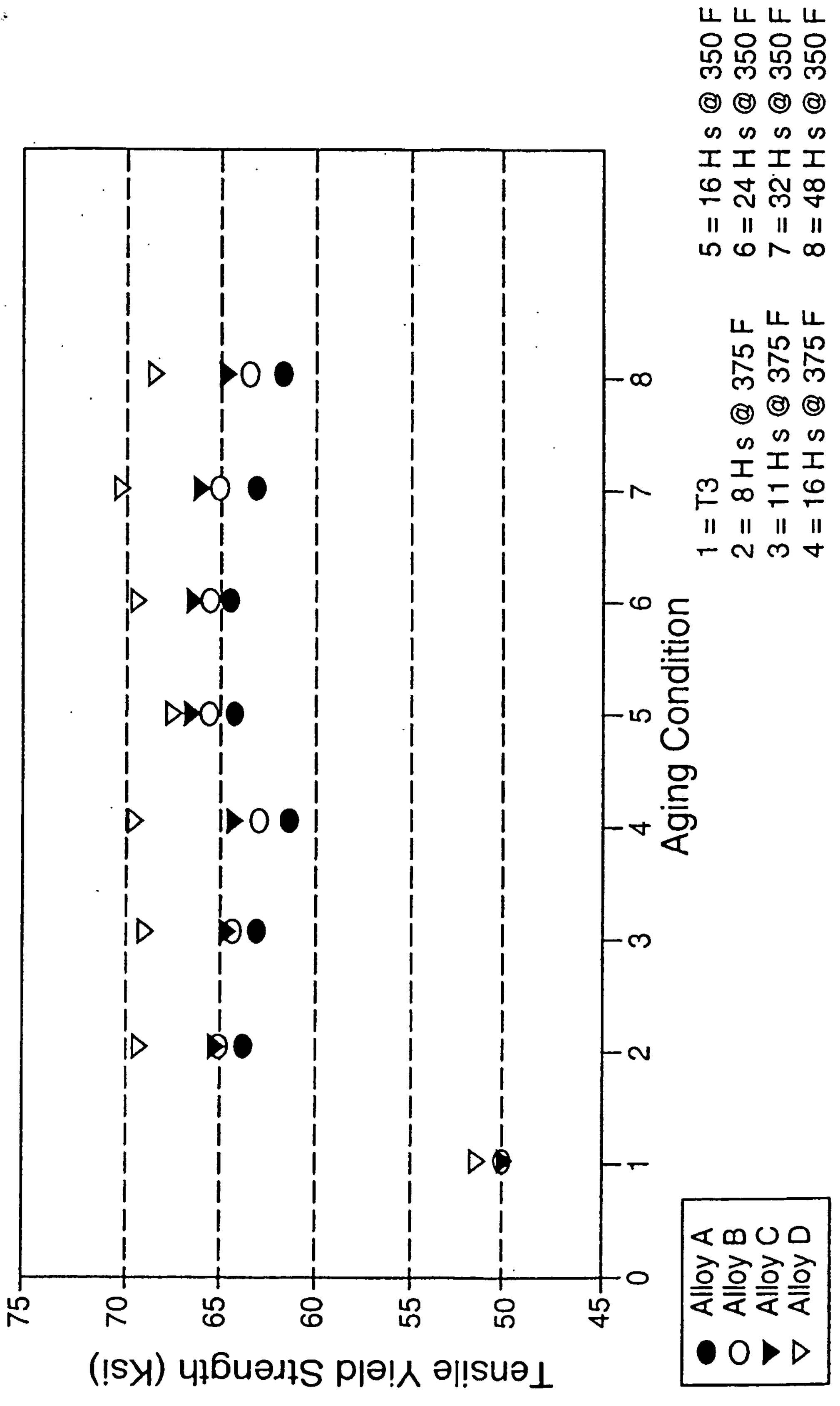

Tensile Yield Strength (Ksi)
75
70
65
60
55
50
45
Aging Condition
0
1
2
3
4
5
6
7
8
● Alloy A
○ Alloy B
▶ Alloy C
▷ Alloy D
1 = T3
2 = 8 Hs @ 375 F
3 = 11 Hs @ 375 F
4 = 16 Hs @ 375 F
5 = 16 Hs @ 350 F
6 = 24 Hs @ 350 F
7 = 32 Hs @ 350 F
8 = 48 Hs @ 350 F

FIG. 6

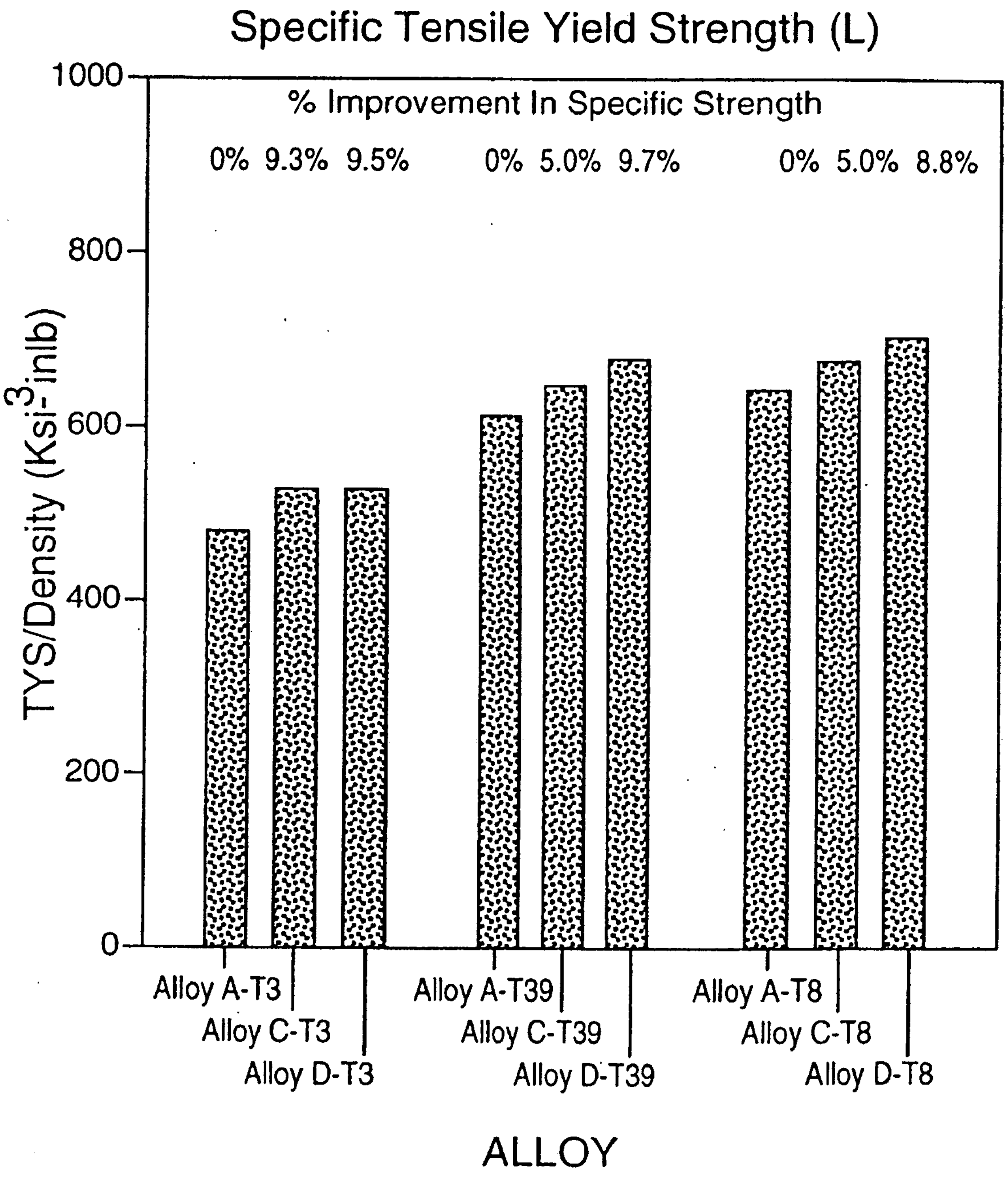

Specific Tensile Yield Strength (L)
% Improvement In Specific Strength
0% 9.3% 9.5%
0% 5.0% 9.7%
0% 5.0% 8.8%
TYS/Density (Ksi-^{3}-inlb)
1000
800
600
400
200
0
Alloy A-T3
Alloy C-T3
Alloy D-T3
Alloy A-T39
Alloy C-T39
Alloy D-T39
Alloy A-T8
Alloy C-T8
Alloy D-T8
ALLOY

FIG. 7

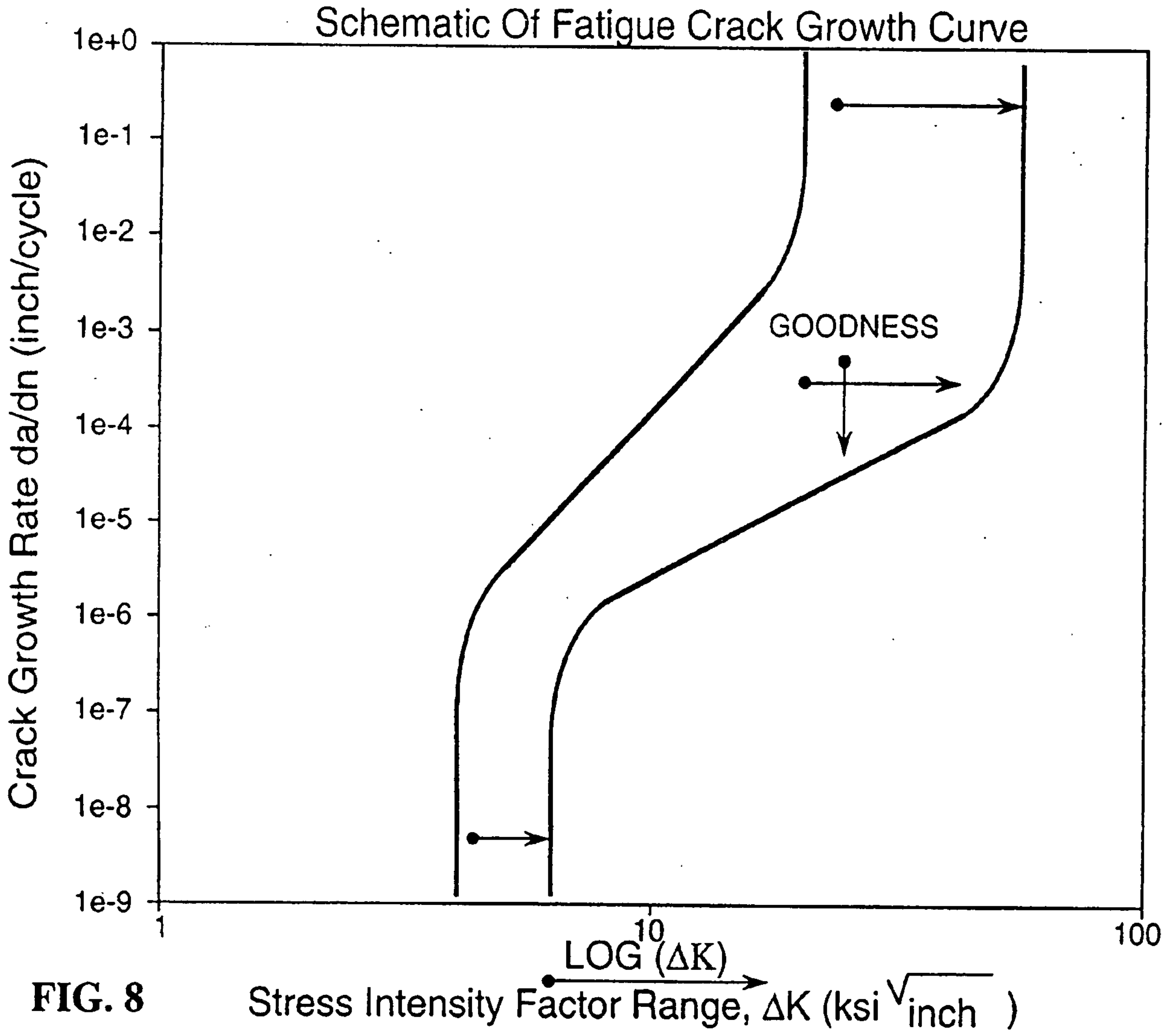

Schematic Of Fatigue Crack Growth Curve
Crack Growth Rate da/dn (inch/cycle)
1e+0
1e-1
1e-2
1e-3
1e-4
1e-5
1e-6
1e-7
1e-8
1e-9
GOODNESS
1
10
100
LOG(ΔK)
10
Stress Intensity Factor Range, ΔK (ksi √inch)

FIG. 8

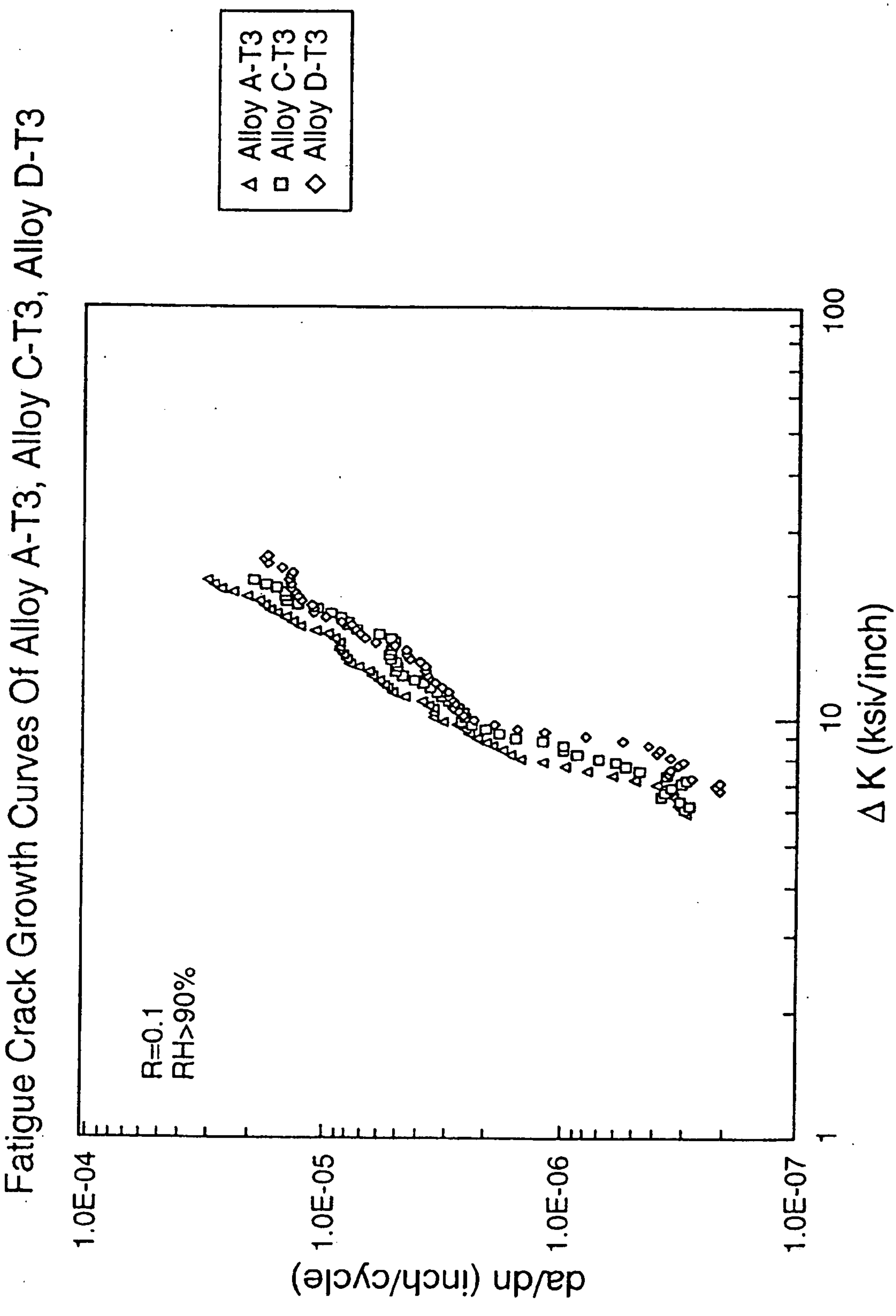

Fatigue Crack Growth Curves Of Alloy A-T3, Alloy C-T3, Alloy D-T3
△ Alloy A-T3
□ Alloy C-T3
◇ Alloy D-T3
R=0.1
RH>90%
da/dn (inch/cycle)
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1
10
100
Δ K (ksi√inch)

FIG. 9

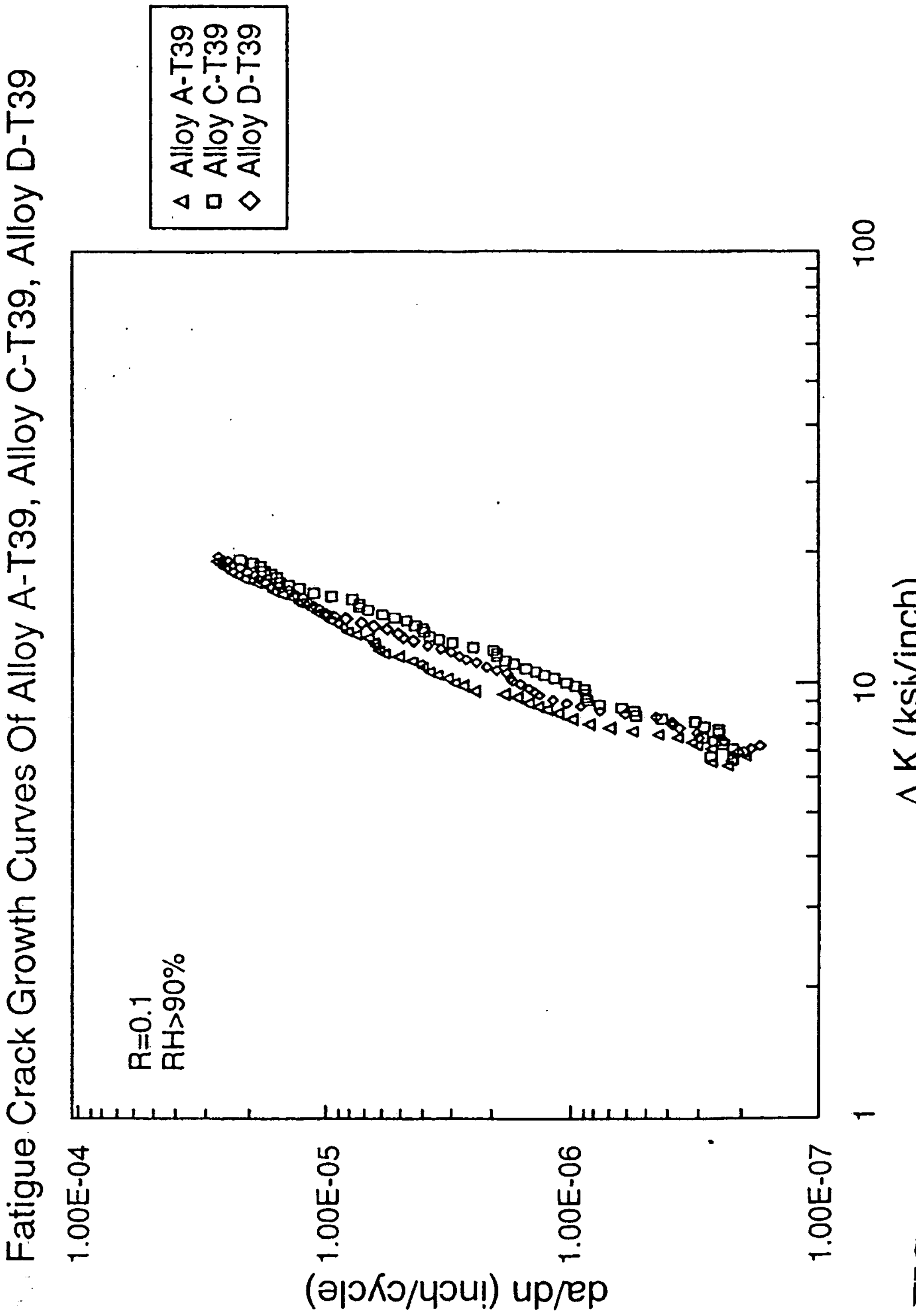

Fatigue Crack Growth Curves Of Alloy A-T39, Alloy C-T39, Alloy D-T39
△ Alloy A-T39
□ Alloy C-T39
◇ Alloy D-T39
R=0.1
RH>90%
da/dn (inch/cycle)
1.00E-04
1.00E-05
1.00E-06
1.00E-07
Δ K (ksi√inch)
1
10
100

FIG. 10

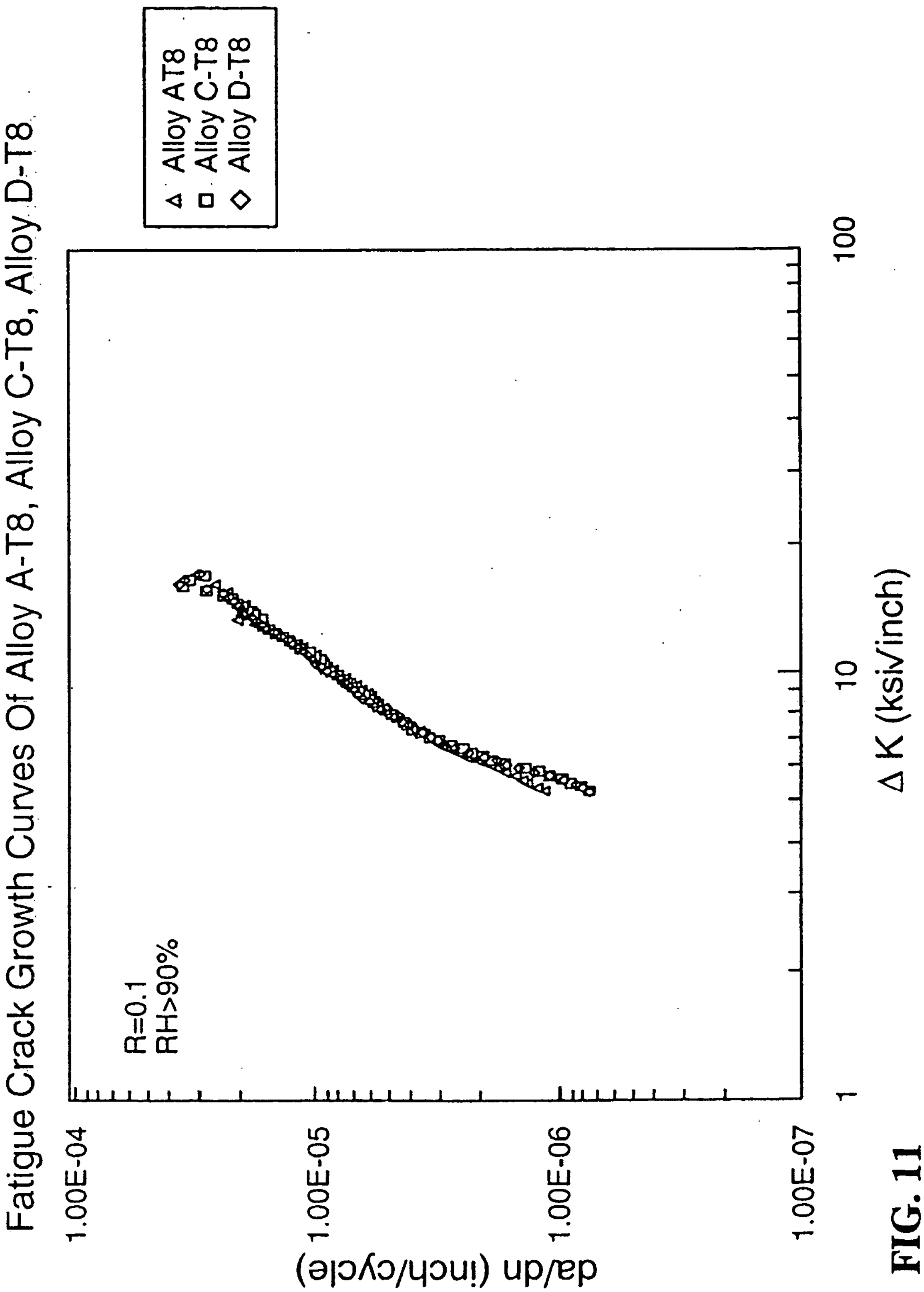

Fatigue Crack Growth Curves Of Alloy A-T8, Alloy C-T8, Alloy D-T8
△ Alloy AT8
□ Alloy C-T8
◇ Alloy D-T8
R=0.1
RH>90%
1.00E-04
1.00E-05
1.00E-06
1.00E-07
da/dn (inch/cycle)
1
10
100
Δ K (ksi√inch)

FIG. 11

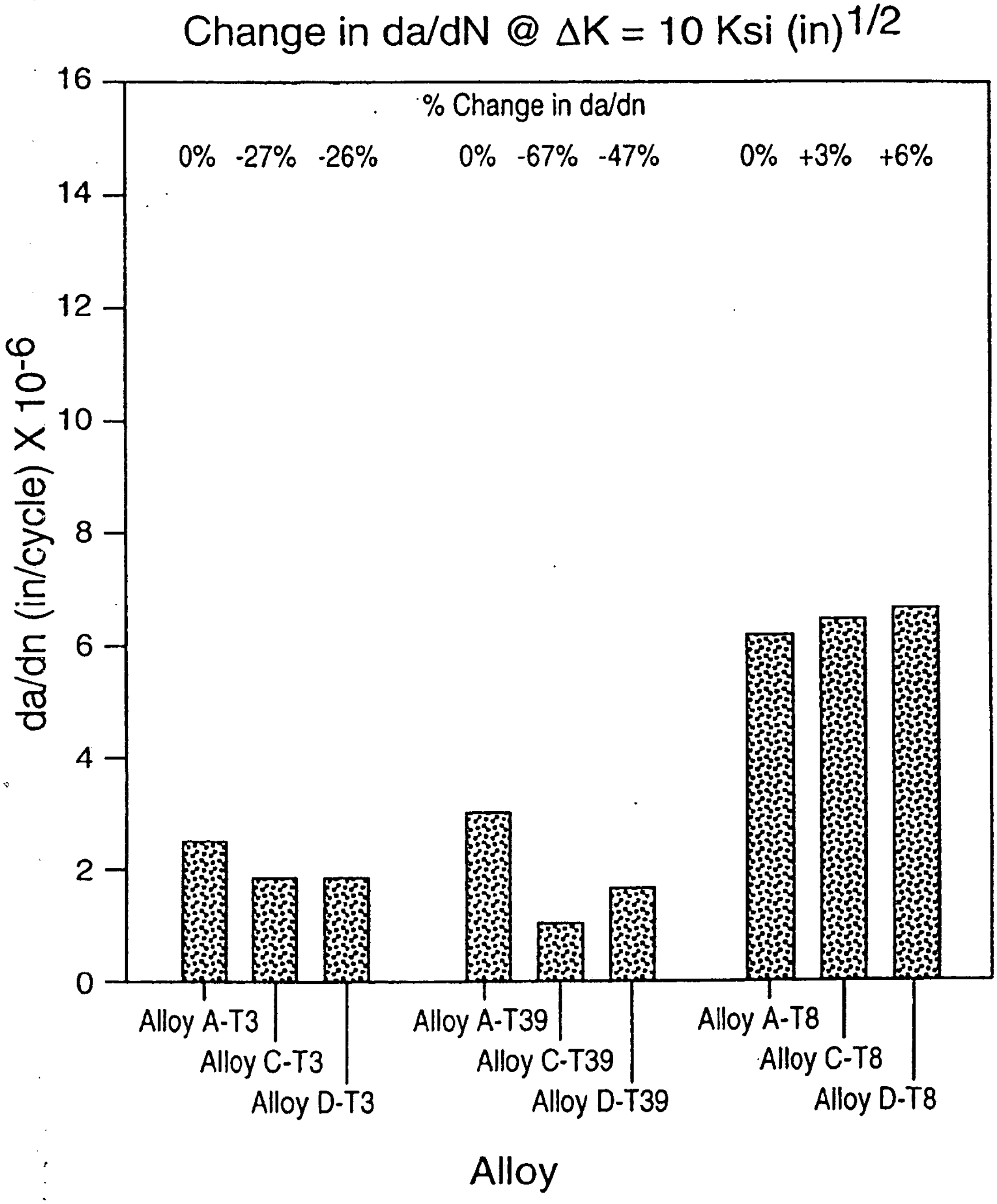
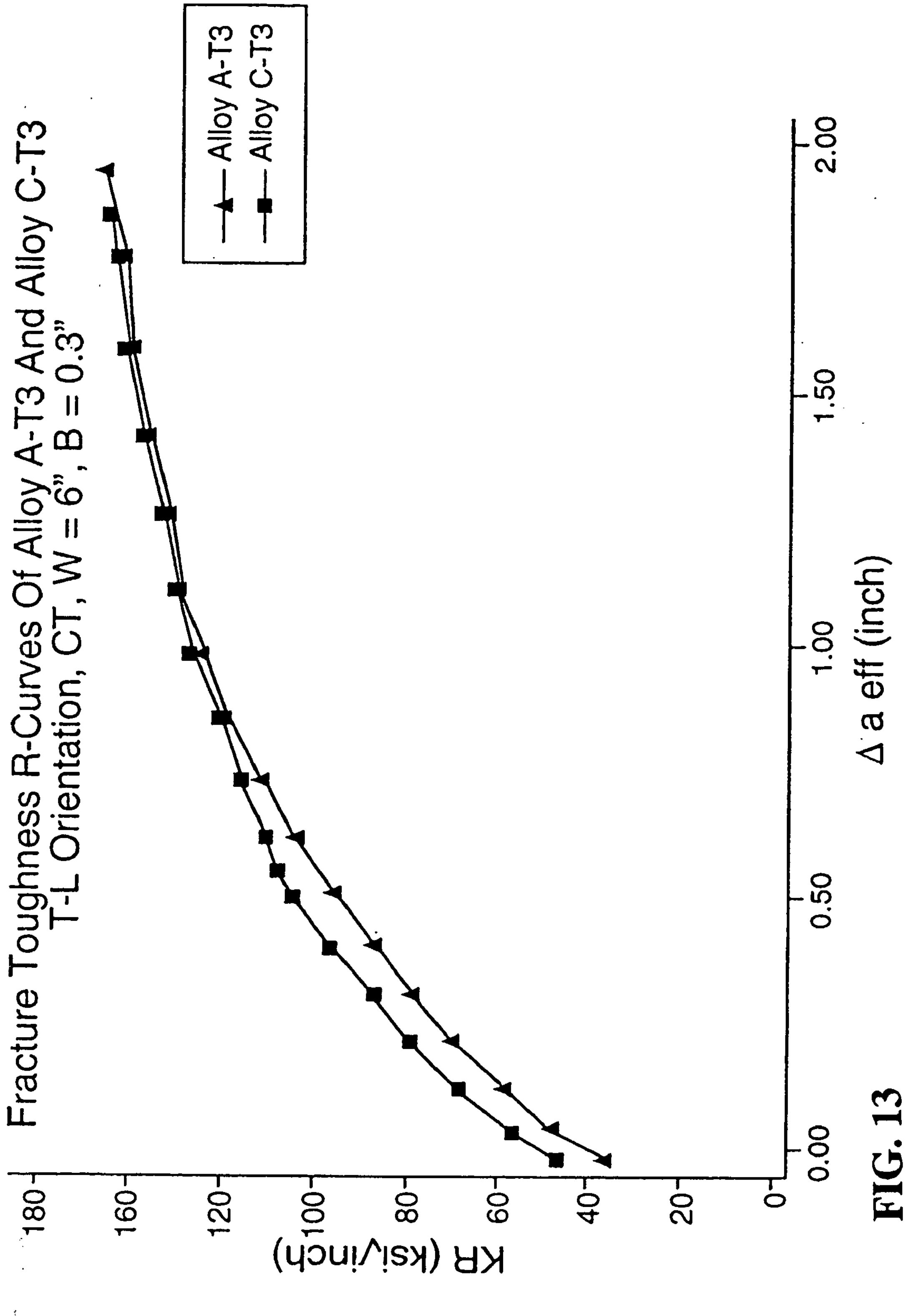

Change in da/dN @ ΔK = 10 Ksi (in)1/2
% Change in da/dn
0%
-27%
-26%
0%
-67%
-47%
0%
+3%
+6%
da/dn (in/cycle) X 10-6
16
14
12
10
8
6
4
2
0
Alloy A-T3
Alloy C-T3
Alloy D-T3
Alloy A-T39
Alloy C-T39
Alloy D-T39
Alloy A-T8
Alloy C-T8
Alloy D-T8
Alloy

FIG. 12



Fracture Toughness R-Curves Of Alloy A-T3 And Alloy C-T3
T-L Orientation, CT, W = 6", B = 0.3"

FIG. 13

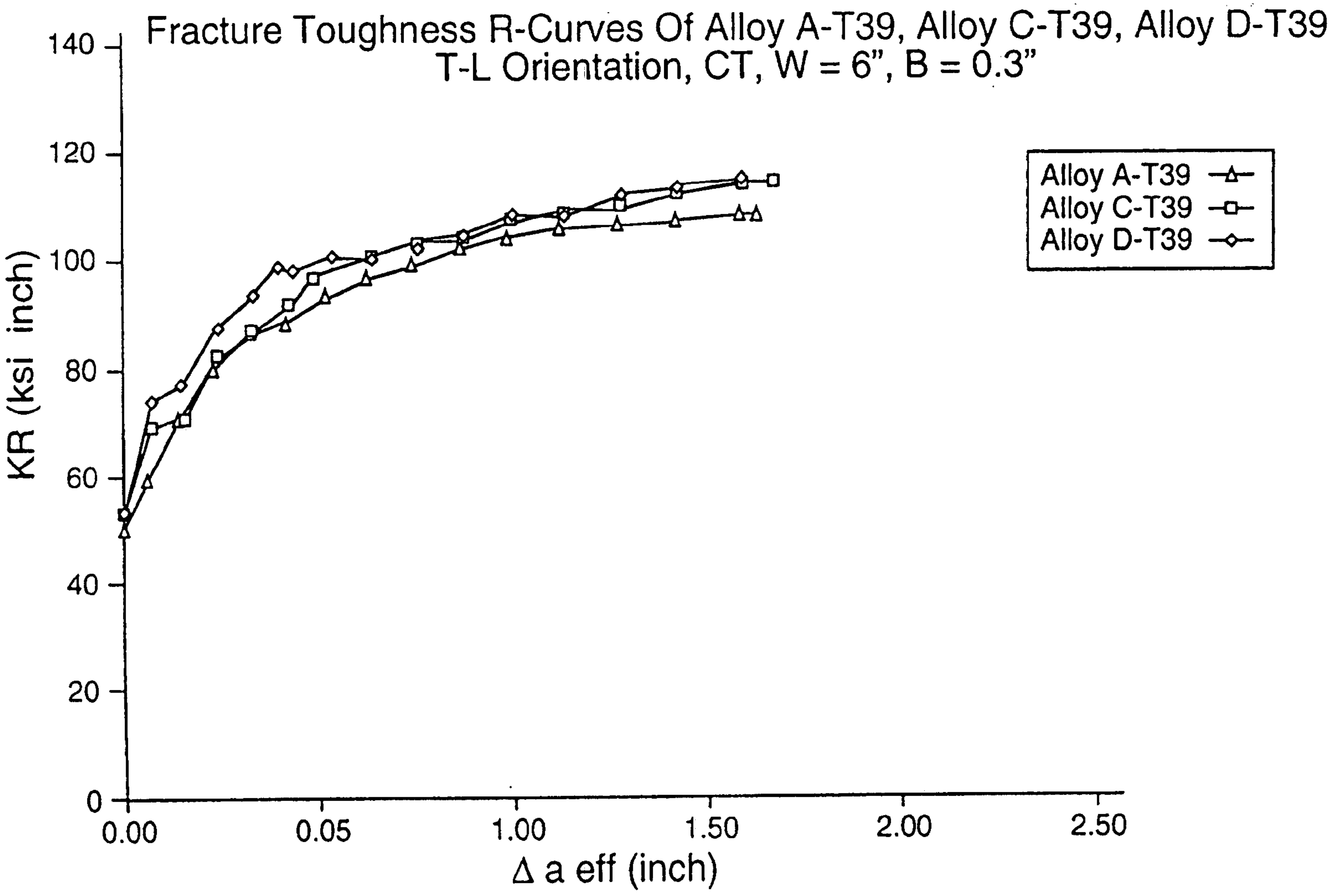

Fracture Toughness R-Curves Of Alloy A-T39, Alloy C-T39, Alloy D-T39
T-L Orientation, CT, W = 6", B = 0.3"

FIG. 14

ALUMINUM-COPPER-MAGNESIUM ALLOYS HAVING ANCILLARY ADDITIONS OF LITHIUM

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. application Ser. No. 09/104,123 filed Jun. 24, 1998, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to aluminum alloys useful in aerospace applications, and more particularly relates to aluminum-copper-magnesium alloys having ancillary additions of lithium which possess improved combinations of fracture toughness and strength, as well as improved fatigue crack growth resistance.

BACKGROUND OF THE INVENTION

[0003] It is generally well known in the aerospace industry that one of the most effective ways to reduce the weight of an aircraft is to reduce the density of aluminum alloys used in aircraft construction. This desire led to the addition of lithium, the lowest density metal element, to aluminum alloys. Aluminum Association alloys, such as 2090 and 2091 contain about 2.0 weight percent lithium, which translates into about a 7 percent weight savings over alloys containing no lithium. Aluminum alloys 2094 and 2095 contain about 1.2 weight percent lithium. Another aluminum alloy, 8090 contains about 2.5 weight percent lithium, which translates into an almost 10 percent weight savings over alloys without lithium.

[0004] However, casting of such conventional alloys containing relatively high amounts of lithium is difficult. Furthermore, the combined strength and fracture toughness of such alloys is not optimal. A tradeoff exists with conventional aluminum-lithium alloys in which fracture toughness decreases with increasing strength.

[0005] Another important characteristic of aerospace aluminum alloys is fatigue crack growth resistance. For example, in damage tolerant applications in aircraft, increased fatigue crack growth resistance is desirable. Better fatigue crack growth resistance means that cracks will grow slower, thus making airplanes much safer because small cracks can be detected before they achieve critical size for catastrophic propagation. Furthermore, slower crack growth can have an economic benefit due to the fact that longer inspection intervals can be utilized.

[0006] A need therefore exists for an aluminum alloy that is useful in aircraft application which has high fracture toughness, high strength and excellent fatigue crack growth resistance.

SUMMARY OF THE INVENTION

[0007] The present invention provides aluminum alloys comprising from about 3 to about 5 weight percent copper; from about 0.5 to about 2 weight percent magnesium; and from about 0.01 to about 0.9 weight percent lithium. It has been found that ancillary additions of low levels of lithium to aluminum alloys having controlled amounts of copper and magnesium provide a high fracture toughness and high strength material which also exhibits equivalent or improved fatigue crack growth resistance over prior art aluminum-copper-magnesium alloys. An aspect of the present invention is to provide an aluminum alloy comprising from about 3 to about 5 weight percent Cu, from about 0.5 to about 2 weight percent Mg, and from about 0.01 to about 0.9 weight percent Li, wherein the Cu and Mg are present in the alloy in a total amount below a solubility limit of the alloy.

[0008] This and other aspects of the present invention will be more apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] **FIG. 1** is a graph of Mg content versus Cu content, illustrating maximum limits of those elements for Al-Cu-Mg-Li alloys in accordance with embodiments of the present invention.

[0010] **FIG. 2** is a graph of fracture toughness (K_Q) and elongation properties versus lithium content for Al-Cu-Mg based alloys in the form of plate products having varying amounts of Li.

[0011] **FIG. 3** is a graph of fracture toughness (K_Q) and tensile yield strength properties versus lithium content for Al-Cu-Mg based alloys in the form of plate products having varying amounts of Li.

[0012] **FIG. 4** is a graph of fracture toughness (K_c and K_{app}) and tensile yield strength properties versus lithium content for Al-Cu-Mg based alloys in the form of sheet products having varying amounts of Li.

[0013] **FIG. 5** is a plot of the fracture toughness and tensile yield strength values shown in **FIG. 4** in comparison with plant typical and minimum fracture toughness and yield strength values for conventional alloy 2524 sheet.

[0014] **FIG. 6** is a chart showing the tensile yield strength of various specimens made from Al-Cu-Mg alloys with various amounts of Li designated Alloy A, Alloy B, Alloy C, and Alloy D after being subjected to different aging conditions.

[0015] **FIG. 7** is a bar graph showing the improvement in specific strength for some of the specimens shown in **FIG. 6**.

[0016] **FIG. 8** is a graph showing the typical representation of fatigue crack growth rate, da/dN (in/cycle) and how it changes.

[0017] **FIG. 9** is a graph showing the fatigue crack growth curves for Alloy A-T3 plate; Alloy C-T3 plate; and Alloy D-T3 plate.

[0018] **FIG. 10** is a graph showing the fatigue crack growth curves for Alloy A-T39 plate; Alloy C-T39 plate; and Alloy D-T39 plate.

[0019] **FIG. 11** is a graph showing the fatigue growth curves for Alloy A-T8 plate; Alloy C-T8 plate; and Alloy D-T8 plate.

[0020] **FIG. 12** is a bar graph showing the percentage change in da/dN at $\Delta K=10$ Ksi $(in)^{1/2}$.

[0021] **FIG. 13** is a graph showing the fracture toughness R-curves of Alloy A-T3 and Alloy C-T3.

[0022] **FIG. 14** is a graph showing the fracture toughness R-curves for Alloy A-T39, Alloy C-T39 and Alloy D-T39 plate.

DETAILED DESCRIPTION

[0023] For the description of alloy compositions herein, all references are to weight percentages unless otherwise indicated. When referring to any numerical range of values, such ranges are to be understood to include each and every number and/or fraction between the stated range minimum and maximum.

[0024] As used herein, the term "about" when used to describe a compositional range or amount of an alloying addition means that the actual amount of the alloying addition may vary from the nominal intended amount due to factors such as standard processing variations as understood by those skilled in the art.

[0025] The term "substantially free" means having no significant amount of that component purposely added to the alloy composition, it being understood that trace amounts of incidental elements and/or impurities may find their way into a desired end product.

[0026] The term "solubility limit" means the maximum amount of alloying additions that can be made to the aluminum alloy while remaining as a solid solution in the alloy at a given temperature. For example, the solubility limit for the combined amount of Cu and Mg is the point at which the Cu and/or Mg no longer remain as a solid solution in the aluminum alloy at a given temperature. The temperature may be chosen to represent a practical compromise between thermodynamic phase diagram data and furnace controls in a manufacturing environment.

[0027] The term "improved combination of fracture toughness and strength" means that the present alloys either possess higher fracture toughness and equivalent or higher strength, or possess higher strength and equivalent or higher fracture toughness, in at least one temper in comparison with similar alloys having no lithium or greater amounts of lithium.

[0028] As used herein, the term "damage tolerant aircraft part" means any aircraft or aerospace part which is designed to ensure that its crack growth life is greater than any accumulation of service loads which could drive a crack to a critical size resulting in catastrophic failure. Damage tolerance design is used for most of the primary structure in a transport category airframe, including but not limited to fuselage panels, wings, wing boxes, horizontal and vertical stabilizers, pressure bulkheads, and door and window frames. In inspectable areas, damage tolerance is typically achieved by redundant designs for which the inspection intervals are set to provide at least two inspections per number of flights or flight hours it would take a visually detectable crack to grow to its critical size.

[0029] The present invention relates to aluminum-copper-magnesium alloys having ancillary additions of lithium. In accordance with the invention, wrought aluminum-copper-magnesium alloys are provided which have improved combinations of fracture toughness and strength over prior art aluminum-copper-magnesium alloys. The present alloys also possess improved fatigue crack growth resistance. The alloys of the present invention are especially useful for aircraft parts requiring high damage tolerance, such as lower wing components including thin plate for skins and extrusions for stringers for use in built-up structure, or thicker plate or extrusions for stiffened panels for use in integral structure; fuselage components including sheet and thin plate for skins, extrusions for stringers and frames, for use in built-up, integral or welded designs. They may also be useful for spar and rib components including thin and thick plate and extrusions for built-up or integral design or for empennage components including those from sheet, plate and extrusion, as well as aircraft components made from forgings including aircraft wheels, spars and landing gear components. The strength capabilities of the alloys are such that they may also be useful for upper wing components and other applications where aluminum-copper-magnesium-zinc alloys are typically employed. The addition of low levels of lithium avoids problems associated with higher (i.e., over 1.5 weight percent lithium) additions of lithium, such as explosions of the molten metal during the casting of ingots.

[0030] In accordance with embodiments of the present invention, the aluminum alloy may be provided in the form of sheet or plate. Sheet products include rolled aluminum products having thicknesses of from about 0.006 to about 0.25 inch. The thickness of the sheet is preferably from about 0.025 to about 0.25 inch, more preferably from about 0.05 to about 0.25 inch. For many applications such as some aircraft fuselages, the sheet is preferably from about 0.05 to about 0.25 inch thick, more preferably from about 0.05 to about 0.2 inch. Plate products include rolled aluminum products having thicknesses of from about 0.25 to about 8 inch. For wing applications, the plate is typically from about 0.50 to about 4 inch. In addition, light gauge plate ranging from 0.25 to 0.50 inch is also used in fuselage applications. The sheet and light gauge plate may be unclad or clad, with preferred cladding layer thicknesses of from about 1 to about 5 percent of the thickness of the sheet or plate. In addition to sheet and plate products, the present alloys may be fabricated as other types of wrought products, such as extrusion and forgings by conventional techniques.

[0031] The compositional ranges of the main alloying elements (copper, magnesium and lithium) of the improved alloys of the invention are listed in Table 1.

TABLE 1

Copper, Magnesium and Lithium Compositional Ranges

	Cu	Mg	Li	Al
Typical	3–5	0.5–2	0.01–0.9	balance
Preferred	3.5–4.5	0.6–1.5	0.1–0.8	balance
More Preferred	3.6–4.4	0.7–1	0.2–0.7	balance

[0032] Copper is added to increase the strength of the aluminum base alloy. Care must be taken, however, to not add too much copper since the corrosion resistance can be reduced. Also, copper additions beyond maximum solubility can lead to low fracture toughness and low damage tolerance.

[0033] Magnesium is added to provide strength and reduce density. Care should be taken, however, to not add too much magnesium since magnesium additions beyond maximum solubility will lead to low fracture toughness and low damage tolerance.

[0034] In accordance with the present invention, the total amount of Cu and Mg added to the alloy is kept below the solubility limits shown in **FIG. 1**. In **FIG. 1**, the typical Cu and Mg compositional ranges listed in Table 1 are shown with a first solubility limit (1), and a second solubility limit (2), for the combination of Cu and Mg contained in the alloy. The solubility limit may decrease, e.g., from the first (1) to the second (2) solubility limit, as the amount of other alloying additions is increased. For example, additions of Li, Ag and/or Zn may tend to lower the solubility limit of Cu and Mg.

[0035] In order to remain below the solubility limit, the amount of Cu and Mg should conform to the formula: $Cu \leqq 2-0.676(Mg-6)$. Preferably, the amount of Cu and Mg conforms to the formula: $Cu \leqq 1.5-0.556(Mg-6)$ when about 0.8 wt % Li is added.

[0036] The amounts of copper and magnesium are thus controlled such that they are soluble in the alloy. This is important in that atoms of the alloying elements in solid solution or which form clusters of atoms of solute may translate to increased fatigue crack growth resistance. Furthermore, the combination of copper, magnesium and lithium needs to be controlled as to not exceed maximum solubility.

[0037] Within the controlled copper and magnesium ranges, the range of the lithium content may be from about 0.01 to 0.9 weight percent, preferably from about 0.1 or 0.2 weight percent up to about 0.7 or 0.8 weight percent. In accordance with the present invention, relatively small amounts of lithium have been found to significantly increase fracture toughness and strength of the alloys as well as provided increased fatigue crack growth resistance and decreased density. However, at lithium levels above the present levels, fracture toughness decreases significantly. Furthermore, care should be taken in not adding too much lithium since exceeding the maximum solubility will lead to low fracture toughness and low damage tolerances. Lithium additions in amounts of about 1.5 weight percent and above result in the formation of the δ' ("delta prime") phase with composition of Al_3Li. The presence of this phase, Al_3Li, is to be avoided in the alloys of the present invention.

[0038] While not intending to be bound by any particular theory, the interaction of lithium atoms in supersaturated solid solution, with atoms of magnesium and/or copper appear to give rise to the formation of clusters of atoms of solute in a W or T3 tempers. This behavior is observed by the appearance of diffuse scatter in electron diffraction images. This behavior may be a contributor for the improvements in fatigue performance of the alloys of the invention.

[0039] In addition to aluminum, copper, magnesium and lithium, the alloys of the present invention can contain at least one dispersoid-forming element selected from chromium, vanadium, titanium, zirconium, manganese, nickel, iron, hafnium, scandium and rare earths in a total amount of from about 0.05 to about 1 weight percent. For example, manganese may be present in a preferred amount of from about 0.2 to about 0.7 weight percent.

[0040] Other alloying elements, such as zinc, silver and/or silicon in amounts up to about 2 weight percent may optionally be added. For example, zinc in an amount of from about 0.05 to about 2 weight percent may be added, typically from about 0.2 to about 1 weight percent. As a particular example, zinc in an amount of 0.5 weight percent may be added. When zinc is added to the alloy, it may serve as a partial or total replacement for magnesium.

[0041] Silver in an amount of from about 0.01 to about 2 weight percent may be added, typically from about 0.05 to about 0.6 weight percent. For example, silver in an amount of from about 0.1 to about 0.4 weight percent may be added.

[0042] Silicon in an amount of from about 0.1 to about 2 weight percent may be added, typically from about 0.3 to about 1 weight percent.

[0043] In accordance with embodiments of the present invention, certain elements may be excluded from the alloy compositions, i.e., the elements are not purposefully added to the alloys, but may be present as unintentional or unavoidable impurities. Thus, the alloys may be substantially free of elements such as Sc, Ag and/or Zn, if desired.

[0044] It has been found that the combination of lower copper levels, higher magnesium levels and lower levels of lithium produce an aluminum alloy that has increased fracture toughness and strength, superior fatigue crack growth resistance and relatively low density. Fracture toughness and strength are critical properties for aluminum alloys used in aircraft applications. Fatigue crack growth resistance is also a critical property for damage tolerant aircraft parts, such as fuselage sections and lower wing sections. As is known, these parts of an aircraft are subject to cyclical stresses, such as the fuselage skin which is expanded and contracted upon pressurization and depressurization of the aircraft cabin and the lower wing skin which experiences tensile stresses in flight and compressive stresses while the aircraft is on the ground. Improved fatigue crack growth resistance means cracks will grow and reach their critical dimension more slowly. This allows longer inspection intervals to be used, thus reducing aircraft operating cost. Alternatively, the applied stress could be raised while keeping the same inspection interval, thereby reducing aircraft weight.

[0045] The following examples illustrate various aspects of the invention and are not intended to limit the scope of the invention.

EXAMPLE 1

[0046] Five Al-Cu-Mg based alloys with varying amounts of Li having compositions as listed in Table 2 were cast as ingots.

TABLE 2

Measured Compositions of Cast Ingots

Alloy No.	Cu	Mg	Li	Ag	Mn	Zr	Si	Fe
1	4.0	0.76	—	0.49	0.3	0.11	0.06	0.04
2	3.9	0.74	0.19	0.49	0.3	0.11	0.02	0.03
3	4.0	0.79	0.49	0.50	0.3	0.11	0.02	0.03
4	4.1	0.75	0.70	0.50	0.3	0.11	0.02	0.03
5	4.1	0.78	1.20	0.50	0.3	0.11	0.02	0.03

[0047] The ingots listed in Table 2 were then fabricated into plate and sheet. Based on calorimetric analyses, the ingots were homogenized as follows. For alloys 1, 2 and 3: the ingots were heated at 50° F./hr to 905° F. (16 hours), then soaked at 905° F. for 4 hours, then heated in 2 hours to 970° F. and soaked for 24 hours. Finally, the ingots were air cooled to room temperature. For alloys 4 and 5: the ingots were heated at 50° F./hour to 905° F. (16 hours), soaked at 905° F. for 8 hours, then heated in 2 hours to 940° F. and soaked for 48 hours prior to air cooled to room temperature.

[0048] All ingots were the heated to 940° F., and hot rolled at about 900° F. Re-heats at 940° F. were provided to keep the metal temperature above 750° F. Rolling parameters were controlled to provide about a 0.5 inch bite reductions. Plate product with 0.7 inch and 0.5 inch gauges was fabricated. In addition, sheet product was hot rolled to a 0.10 inch gauge.

[0049] For alloys 1, 2 and 3, samples were solution heat treated (SHT) at a temperature of 970 F. Plate pieces were SHT for 2 hours. Sheet samples got a soak of only 1 hour. For alloys 4 and 5, samples were solution heat treated at a temperature of 940° F. Plate pieces were SHT for 2 hours. Sheet samples got a soak of only 1 hour.

[0050] All samples were quenched in water at room temperature and stretched 4% prior to aging to reach a T3 temper. All samples were aged at 310° F. for 24 hours to reach a T8-type temper.

[0051] Fracture toughness (K_{Ic} or K_Q), ultimate tensile strength, tensile yield strength and elongation (4D) of the 0.5 inch gauge plate were measured. Tensile tests were performed in the longitudinal direction in accordance with ASTM B 557 "Standard Test Methods of Tension Testing of Wrought and Cast Aluminum and Magnesium-Alloy Products" on round specimens 0.350 inch in diameter. Fracture toughness was measured in the L-T orientation in accordance with ASTM E399-90 "Standard Test Method for Plane Strain Fracture Toughness of Metallic Materials" supplemented by ASTM B645-02 "Standard Practice for Plane Strain Fracture Toughness of Aluminum Alloys." The test specimens used were of full plate thickness and the W dimension was 1.0 inch. The results are listed in Table 3 and shown in **FIGS. 2 and 3**. Only the test results from Alloy 5 satisfied the validity requirements in ASTM E399-90 for a valid K_{Ic}. The test results from Alloys 1-4 failed to meet the following validity criteria: (1) $B \geqq 2.5(K_Q/\sigma_{ys})^2$; (2) $a \geqq 2.5(K_Q/\sigma_{ys})^2$; and (3) $P_{max}/P_Q \leqq 1.1$, where B, K_Q, σ_{ys}, P_{max}, and P_Q are as defined in ASTM E399-90. The remaining validity criteria were all met. Test results not meeting the validity criteria are designated K_Q, the designation K_{Ic} being reserved for test results meeting all the validity criteria. Failure to satisfy the above three criteria indicates that the specimen thickness was insufficient to achieve linear-elastic, plane-strain conditions as defined in ASTM E399. Those skilled in the art will appreciate that the higher the toughness or the lower the yield strength of the product the greater the thickness and width required to satisfy the above three criteria and achieve a valid result, K_{Ic}. The specimen thickness in these tests was necessarily limited by the plate thickness. A valid K_{Ic} is generally considered a material property relatively independent of specimen size and geometry. Those skilled in the art will appreciate that K_Q values, while they may provide a useful measure of material fracture toughness as in this case, can vary significantly with specimen size and geometry. Therefore, in comparing K_Q values from different alloys it is imperative that the comparison be made on the basis of a common specimen size as was done in these tests. K_Q values from specimens of insufficient thickness and width to meet the above validity criteria are typically lower than a valid K_{Ic} coming from a larger specimen.

TABLE 3

Measured Properties from Plate

Alloy No.	Li amount (wt %)	TYS (ksi)	UTS (ksi)	Elongation (%)	Toughness-K_Q (ksi √ in)
1	0	66.1	70.3	15.7	37
1	0	65.9	70.1	16.4	37.4
2	0.19	68.6	72.4	17.1	42.3
2	0.19	68.4	72.4	17.1	41.3
3	0.49	76.4	79.6	15	40.3
3	0.49	76.8	79.7	14.3	39.8
4	0.70	80.6	84.5	12.9	39
4	0.70	80.6	84.4	12.9	40.6
5	1.20	85.9	90	8.6	26.5 (K_{Ic})
5	1.20	85.7	89.9	8.6	25.6

[0052] Fracture toughness (K_c and K_{app}) in the L-T orientation and tensile yield strength in the L orientation were measured for 0.150 inch gauge sheet. The tests were performed in accordance with ASTM E561-98 "Standard Practice for R-Curve Determination" supplemented by ASTM B646-97 "Standard Practice for Fracture Toughness Testing of Aluminum Alloys". The test specimen was a middle-cracked tension M(T) specimen of full sheet thickness having a width of 16 inches, an overall length of 44 inches with approximately 38 inches between the grips, and an initial crack length, $2a_o$, of 4 inches. K_c was calculated in accordance with ASTM B646 and K_{app} in accordance with Mil-Hdbk-5J, "Metallic Materials and Elements for Aerospace Structural Vehicles." The results are shown in Table 4 and **FIG. 4**. It is recognized in the art that K_{app} and K_c, for alloys having high fracture toughness, typically increases as specimen width increases or specimen thickness decreases. K_{app} and K_c are also influenced by initial crack length, $2a_o$, and specimen geometry. Thus K_{app} and K_c values from different alloys can only be reliably compared from test specimens of equivalent geometry, width, thickness and initial crack length as was done in these tests. While the toughness improvements observed in the invention alloys (Alloys 2-4) correspond to a test specimen of the type and dimensions noted, it is expected that similar improvements will be observed in other types and sizes of test specimens, although the values of K_{app} and K_c and the absolute magnitude of the numerical differences may vary for the reasons just stated.

TABLE 4

Measured Properties from Sheet: L orientation

Alloy No.	Li Amount (wt %)	TYS (ksi)	Toughness - K_{app} (ksi√in)	Toughness-K_c (ksi√in)
1	0	63	122	172
2	0.19	69	128	184
3	0.49	77	131	183
4	0.70	80	131	185
5	1.20	90	87	97

[0053] **FIG. 5** is a graph plotting the fracture toughness and longitudinal tensile yield strength values shown in **FIG.**

4 against plant typical and minimum values for conventional alloy 2524 sheet under similar conditions.

[0054] As shown in FIGS. 2-5, the Al-Cu-Mg based alloys of the present invention having Li additions of from 0.2 to 0.7 weight percent possess significantly improved fracture toughness in comparison with similar alloys containing either no Li or a greater amount of Li. In addition, the alloys of the present invention having relatively low levels of lithium achieve significantly improved combinations of fracture toughness and strength.

EXAMPLE 2

[0055] An ingot of an aluminum-copper-magnesium alloy having the following composition was cast (remainder is aluminum and incidental impurities):

INGOT NO. 1

Si	Fe	Cu	Mn	Mg	Zn	Zr
0.03	0.03	3.24	0.58	1.32	0	0.11

[0056] Material fabricated from this ingot is designated Alloy A.

[0057] After this, the remaining molten metal was re-alloyed (i.e., alloying again an alloy already made) by adding 0.25% lithium to create a target addition of 0.25 weight percent lithium. A second ingot was then cast having the following composition (remainder is aluminum and incidental impurities):

INGOT NO. 2

Li	Si	Fe	Cu	Mn	Mg	Zn	Zr
0.19	0.03	0.04	3.41	0.61	1.28	0	0.1

[0058] Material fabricated from this ingot will be designated Alloy B hereinafter in this example.

[0059] Ingot No. 3 was created by re-alloying the remaining molten metal after casting Ingot No. 2 and then adding another 0.25 weight percent lithium to create a total target addition of 0.50 weight percent lithium. Ingot No. 3 had the following composition (remainder is aluminum and incidental impurities):

INGOT NO. 3

Li	Si	Fe	Cu	Mn	Mg	Zn	Zr
0.35	0.04	0.04	3.37	0.6	1.2	0	0.11

[0060] Material fabricated from this ingot will be designated Alloy C hereinafter in this example.

[0061] Ingot No. 4 was created by re-alloying the remaining molten metal after casting Ingot No. 3 and then adding another 0.26 weight percent lithium to create a total target addition of 0.75 weight percent lithium. A fourth ingot was cast having the following composition (remainder is aluminum and incidental impurities):

INGOT NO. 4

Li	Si	Fe	Cu	Mn	Mg	Zn	Zr
0.74	0.02	0.03	3.34	0.56	1.35	0.01	0.12

[0062] Material fabricated from this ingot will be designated Alloy D hereinafter in this example.

[0063] The four ingots were stress relieved and homogenized. The ingots were then subjected to a standard presoak treatment after which the ingots were machine scalped. The scalped ingots were then hot rolled into four (4) separate 0.7 inch gauge plates using hot rolling practices typical of 2XXX alloys.

[0064] After the four separate plates were produced, a section of each of the plates was removed. Each of the four sections were (a) solution heat treated; (b) quenched; and (c) stretched 1.5%. After this, eight tensile strength test samples were produced from each of the treated four (4) sections, making a total of thirty-two tensile strength test samples. One tensile strength test sample from each group of eight (there being a total of four plates in each group) was each subject to eight different aging conditions, as described in the legend of **FIG. 6**. After this, tensile yield strength tests were performed, with the results being shown in **FIG. 6**. It will be seen that the alloys having lithium additions exhibited greater strength than those without lithium, which at the same time exhibiting thermal stability.

[0065] After this, the remainder of three of the four plates (i.e., Ingot No. 1 plate, Ingot No. 3 plate and Ingot No. 4 plate) was each cut into thirds, to form pieces 1, 2 and 3 for each plate, or a total of 9 pieces. Piece 1 of all three plates were (a) solution heat treated; (b) quenched; (c) stretched 1½%; and (d) aged to T8 temper by aging it 24 @350° F. These pieces were designated Alloy A-T8, Alloy C-T8; and Alloy D-T8. Piece 2 of all three plates were (a) solution heat treated; (b) quenched; (c) stretched 1½%; and (d) naturally aged to T3 temper. These pieces were designated Alloy A-T3; Alloy C-T3; and Alloy D-T3. Finally, Piece 3 of all three plates were (a) solution heat treated; (b) quenched; (c) cold rolled 9%; (d) stretched 1½%; and (e) naturally aged. These pieces were designated Alloy A-T39; Alloy C-T39; and Alloy D-T39. It was these pieces which provided the material for all of the further testing which will be reported herein.

[0066] Referring now to **FIG. 7**, the tensile yield strength divided by density for a testing portion of each of the nine pieces produced above is shown. It can be seen that improvements in the tensile yield strength to density ratio were found for ancillary lithium additions.

[0067] Referring now to FIGS. 8-12, the key property of fatigue crack growth resistance will now be discussed. **FIG. 8** is a graph showing the typical representation of fatigue crack growth performance and how improvements therein can be shown. The x-axis of the graph shows the applied driving force for fatigue crack propagation in terms of the stress intensity factor range, ΔK, which is a function of applied stress, crack length and part geometry. The y-axis of the graph shows the material's resistance to the applied driving force and is given in terms of the rate at which a crack propagates, da/dN in inch/cycle. Both ΔK and da/dN are presented on logarithmic scales as is customary. Each curve represents a different alloy with the alloy having the curve to the right exhibiting improved fatigue crack growth resistance with respect to the alloy having the curve to the left. This is because the alloy having the curve to the right exhibits a slower crack propagation rate for a given ΔK which represents the driving force for crack propagation. Fatigue crack growth testing of all alloys in the L-T orientation was performed in accordance with ASTM E647-95a "Standard Test Method for Measurement of Fatigue Crack Growth Rates". The test specimen was a middle-cracked tension M(T) specimen having a width of 4 inches and a thickness of 0.25 inch. The tests were performed in controlled high humidity air having a relative humidity greater than 90% at a frequency of 25 Hz. The initial value of the stress intensity factor range, ΔK, in these tests was about 6 ksi√in and the tests were terminated at a ΔK of about 20 ksi√in.

[0068] Turning to FIGS. **9-11**, it can be seen, that based on the criteria discussed with respect to **FIG. 8**, the addition of lithium substantially increases the fatigue crack growth resistance in the respective alloys in the T3 and T39 conditions. The fatigue crack rates for crack driving forces of ΔK equal to 10 ksi√in are summarized in **FIG. 12**. The percentage improvement in fatigue crack growth resistance (i.e., percentage reduction in fatigue crack growth rates) is given at the top of the graph. Alloy C-T3 and Alloy D-T3 show improvements of 27% and 26%, respectively over Alloy A-T3 (no lithium additions). The percentage improvements in fatigue crack growth resistance of Alloy C-T39 and Alloy C-T39 over Alloy A-T39 (no lithium additions) was 67% and 47%, respectively. Those skilled in the art will appreciate that fatigue crack growth rates may be significantly influenced by humidity level and frequency in moist air environments as a result of an environmental contribution to fatigue crack growth. Thus, while the fatigue crack growth improvements exhibited by the invention alloys correspond to the specific humidity and frequency noted, it is expected that similar improvements will be observed under other testing conditions.

[0069] With regard to the T8 alloys, it can be seen that the lithium additions do not improve the fatigue crack growth resistance. In the case of artificially aged alloys, aged to peak strength, the only advantage of lithium additions is in terms of additional strength and lower density.

[0070] **FIGS. 13 and 14** show the fracture toughness R-curves for the T3 and T39 tempers, respectively, in the T-L orientation. The R-curve is a measure of resistance to fracture (KR) versus stable crack extension (Δaeff). In addition, Table 5 shows single-point measurements of fracture toughness for Alloys A, C and D in the T3, T39 and T8 tempers in terms of K_{R25}, which is the crack extension of resistance, K_R, on the R-curve corresponding to the 25% secant offset of the test record of load versus crack-opening displacement (COD), and K_Q, which is the crack extension resistance correspondence to the 5% secant offset of the test record of load versus COD. K_{R25} is an appropriate measure of fracture toughness for moderate strength, high toughness alloy/tempers such as T3 and T39, which K_Q is appropriate for higher strength, lower toughness alloy/tempers such as T8. The R-curve tests were performed in accordance with ASTM E561-98 "Standard Practice for R-Curve Determination" The test specimen was a compact-tension C(T) specimen having a W dimension of 6 inches, a thickness of 0.3 inches and an initial crack length, a_o, of 2.1 inches. The K_{R25} value was determined from these same tests in accordance with ASTM B646-94 "Standard Practice for Fracture Toughness Testing of Aluminum Alloys". Those skilled in the art will appreciate that K_{R25} values, like K_c and K_{app}, depend on specimen width, thickness and initial crack length and that reliable comparisons between alloys can only be made on test specimens of equivalent dimensions. Plane strain fracture toughness testing was performed in the L-T T orientaion in accordance with ASTM E399-90 supplemented by ASTM B645-95. The test specimens used had a thickness of 0.65 inch and the W dimension was 1.5 inches. The results did not satisfy one or more of the following validity criteria: $B \geqq 2.5(K_Q/\sigma_{ys})^2$; (2) $a \geqq 2.5(K_Q/\sigma_{ys})^2$; and (3) $P_{max}/P_Q < 1.1$, where B, K_Q, σ_{ys}, P_{max}, and P_Q are as defined in ASTM E399-90. The previous discussion regarding K_Q values which are invalid by the the above criteria is also applicable to these results.

TABLE 5

Strength and Toughness Measurements
(Tensile Longitudinal Properties - Toughness Orientation L-T or T-L)

Alloy/Temper	TYS (ksi)	UTS (ksi)	Elongation (%)	K_Q, L-T (ksi√ in)	K_{R25}, T-L (ksi √ in)
Alloy A-T3	47.7	65.6	18.6	—	97.9
Alloy C-T3	51.4	69.8	17.1	—	107.8
Alloy D-T3	51.1	70.6	17.5	—	not tested
Alloy A-T39	61.2	67.3	11.4	—	88.8
Alloy C-T39	63.3	70.7	9.3	—	91.5
Alloy D-T39	65.7	70.5	9.9	—	97.5
Alloy A-T8	63.7	69.7	12.1	32.4	—
Alloy C-T8	65.9	71.9	11.7	38.7	—
Alloy D-T8	67.8	73.8	10.7	38.9	—

[0071] It will be appreciated that fracture toughness is significantly improved by the low levels of lithium additions in accordance with the present invention, in comparison with similar alloys having either no lithium or greater amounts of lithium. Furthermore, the lithium additions of the present invention yield improved toughness at higher strength levels. Therefore, the combination of fracture toughness and strength is significantly improved. This is unexpected because lithium additions are known to decrease fracture toughness in conventional aluminum-copper-magnesium-lithium alloys.

[0072] While specific embodiments of the invention have been disclosed, it will be appreciated by those skilled in the art that various modifications and alterations to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the appended claims and any and all equivalents thereof.

What is claimed is:

1. An aluminum alloy comprising from about 3 to about 5 weight percent Cu, from about 0.5 to about 2 weight

percent Mg, and from about 0.01 to about 0.9 weight percent Li, wherein the Cu and Mg are present in the alloy in a total amount below a solubility limit of the alloy.

2. The aluminum alloy of claim 1, wherein the Li content is from about 0.1 to about 0.8 weight percent.

3. The aluminum alloy of claim 1, wherein the Li content is from about 0.2 to about 0.7 weight percent.

4. The aluminum alloy of claim 1, wherein the Cu content is from about 3.5 to about 4.5 weight percent.

5. The aluminum alloy of claim 1, wherein the Cu content is from about 3.6 to about 4.4 weight percent.

6. The aluminum alloy of claim 1, wherein the Mg content is from about 0.6 to about 1.5 weight percent.

7. The aluminum alloy of claim 1, wherein the Mg content is from about 0.7 to about 1 weight percent.

8. The aluminum alloy of claim 1, wherein the Cu and Mg content conform to the formula: $Cu \leqq 2-0.676(Mg-6)$.

9. The aluminum alloy of claim 1, wherein the Cu and Mg content conform to the formula: $Cu \leqq 1.5-0.556(Mg-6)$.

10. The aluminum alloy of claim 1, further comprising from about 0.01 to about 2 weight percent Ag.

11. The aluminum alloy of claim 10, wherein the Ag content is from about 0.05 to about 0.5 weight percent.

12. The aluminum alloy of claim 10, wherein the Ag content is from about 0.1 to about 0.4 weight percent.

13. The aluminum alloy of claim 1, further comprising from about 0.05 to about 2 weight percent Zn.

14. The aluminum alloy of claim 13, wherein the Zn content is from about 0.2 to about 1 weight percent.

15. The aluminum alloy of claim 13, wherein the Zn content is about 0.5 weight percent.

16. The aluminum alloy of claim 1, further comprising from about 0.1 to about 2 weight percent Si.

17. The aluminum alloy of claim 16, wherein the Si content is from about 0.3 to about 1 weight percent.

18. The aluminum alloy of claim 1, further comprising at least one dispersoid-forming element selected from chromium, vanadium, titanium, zirconium, manganese, nickel, iron, hafnium, scandium and rare earth elements.

19. The aluminum alloy of claim 18, wherein the at least one dispersoid-forming element is present in a total amount up to about 1.0 weight percent of the alloy.

20. The aluminum alloy of claim 1, further comprising from about 0.2 to about 0.7 weight percent Mn.

21. The aluminum alloy of claim 1, wherein the aluminum alloy is in the form of a sheet.

22. The aluminum alloy of claim 1, wherein the aluminum alloy is in the form of a plate.

23. The aluminum alloy of claim 1, wherein the aluminum alloy is in the form of an extrusion.

24. The aluminum alloy of claim 1, wherein the aluminum alloy is in the form of a forging.

* * * * *

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J. T. Staley[1]

Microstructure and Toughness of High-Strength Aluminum Alloys

REFERENCE: Staley, J. T., "**Microstructure and Toughness of High-Strength Aluminum Alloys,**" *Properties Related to Fracture Toughness, ASTM STP 605,* American Society for Testing and Materials, 1976, pp. 71–103.

ABSTRACT: The toughness of wrought, high-strength aluminum alloys is related to the amount, type, and morphology of coarse (larger than about 1 μm) constituent particles, intermediate size (about 0.02 to 0.5 μm) dispersoids, and fine (down to about 0.001 μm) precipitates. High toughness can be attained by minimizing the size and volume fraction of constituent particles, increasing the interdispersoid distance, refining the intragranular precipitate in 2XXX alloys, and controlling the intergranular precipitate in 7XXX alloys. For highest toughness in 7XXX alloy products where low residual stress is desired, rapid quenching followed by the minimum amount of cold work required for mechanical stress relief is recommended.

KEY WORDS: wrought aluminum alloys, fracture properties, toughness, notch sensitivity, tear tests, metallurgical constituents, precipitates, crack propagation

The purpose of this paper is to illustrate the relationship between certain microstructural features and the toughness of wrought, high-strength aluminum alloys and to present examples of alloys developed to have high fracture toughness.

Specimens for determining the fracture toughness of aluminum alloys are not standardized, and different indexes of toughness are employed. A brief review of some toughness indexes is offered before the relationship between microstructure and toughness is discussed. Because of the large number of variables usually studied in any investigation to determine effects of microstructure on fracture toughness, use of large-scale specimens designed to measure the stress intensity factors K_c or K_{Ic} is not feasible. Consequently, smaller and less expensive specimens have been

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developed and are often used in alloy development and improvement programs [*1*][2]. The tear specimen provides two indexes of fracture toughness: (1) energy to propagate a crack and (2) ratio of the tear strength to the yield strength [*2*]. Both of these toughness indicators have been found to correlate with K_c[3] and K_{Ic}[*3*], and for the results presented in this paper both changed qualitatively in the same manner with changes in microstructure. The ratio of the strength determined using a circumferentially notched tension specimen to the yield strength of a smooth tension specimen is also used as an index to toughness [*4*]. This toughness indicator has been found to correlate with K_{Ic}[*3*]. Most of the conclusions presented in the paper were made based on results of tests of these specimens. Some of the conclusions have been verified by K_c and K_{Ic}[4] measurements obtained using center cracked panels and compact tension fracture toughness specimens, respectively. K_c and K_{Ic} values estimated from correlation with the tear or notch tension test data are identified as "estimated" in the figures.

Control of three microstructural features in high-strength aluminum alloys has led to substantial improvements in toughness and short-transverse ductility. These three features can be classified as constituents, dispersoids, and hardening precipitates according to the way in which they form.

Constituent Particles

All commercial 2XXX and 7XXX alloys contain significant amounts of the impurity elements iron and silicon. These elements are in liquid solution, but they combine with the other elements and separate during ingot solidification as coarse constituent particles up to about 30 μm in the longest dimension. These constituent particles are broken up somewhat during subsequent fabrication, but they cannot be taken into solid solution.

In addition to these insoluble constituent particles, most of the high-strength aluminum alloys contain intermetallic constituents which are at least partially soluble and may be as large as the insoluble particles. These constituents are made up of the major alloying elements such as zinc, magnesium, and copper and may be combined with aluminum. In certain of the alloys, these constituent particles cannot be completely dissolved during fabrication or heat treatment because melting is encountered before complete solution can be attained.

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

[3] It is recognized that K_c is not a geometry independent property of the material, but is dependent upon thickness, panel size, and test procedure. All K_c data referred to in this paper were obtained directly from or by correlation of tear tests with tests of 0.063-in.-thick, 16-in.-wide, center cracked panels ($2a/w = 0.25$) without antibuckling guides as described in Ref *3*.

[4] All K_{Ic} data not referred to as "estimated" in this paper were obtained from compact fracture toughness specimens tested in accordance with ASTM Method E 399.

Constituent particles are considered to be detrimental to toughness because they fracture when stressed, thus providing preferential crack paths. Numerous investigations [*5-10*] have demonstrated that decreasing the iron and silicon contents decreases the number of Al_7Cu_2Fe, $FeAl_6$, and Mg_2Si insoluble constituents and increases toughness. An example of the effect of decreasing the iron and silicon contents on the toughness of 2024 sheet is illustrated in Fig. 1, and the results of multiple regression analyses of tear tests of 100 lots of 7050 sheet in Fig. 2 provide more quantitative information of the effect of these elements [*11*]. Thermal mechanical treatments prior to solution heat treatment can also increase toughness by modifying the size, distribution, and volume fraction of the partially soluble constituent particles. For example, decreasing the size of the Al_2CuMg particles in high-purity 2124 sheet from a range of about 10 to 20 μm to a range of about 5 to 10 μm by thermal mechanical treatments

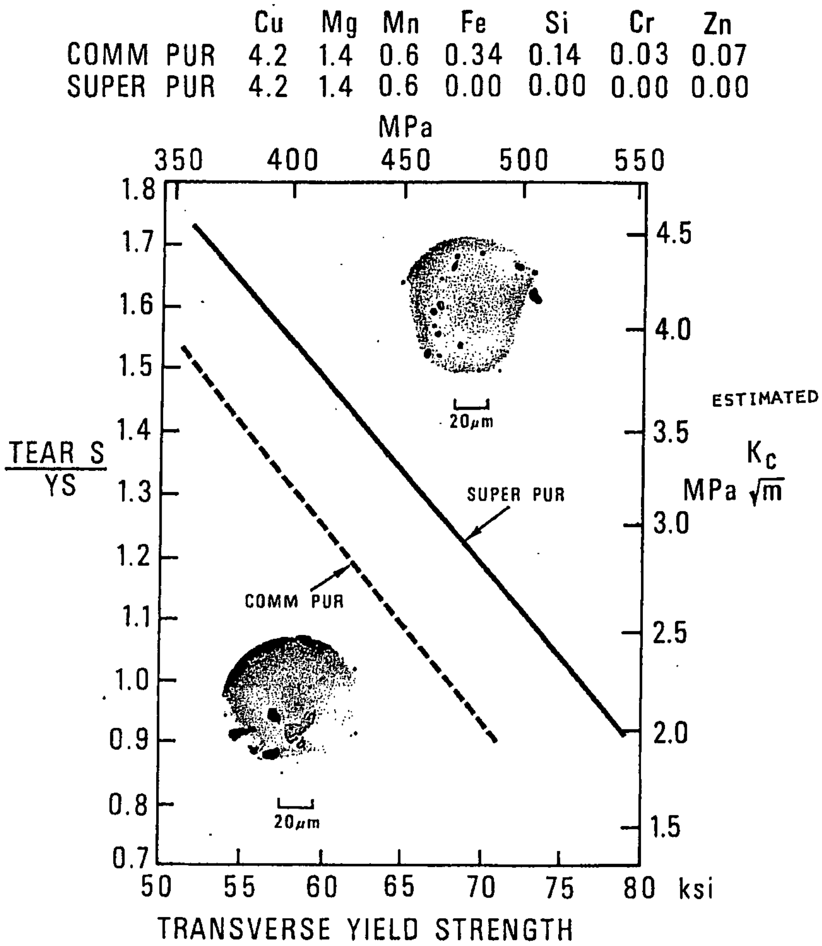


FIG. 1—*Effects of base metal purity on the toughness of 2024 sheet.*

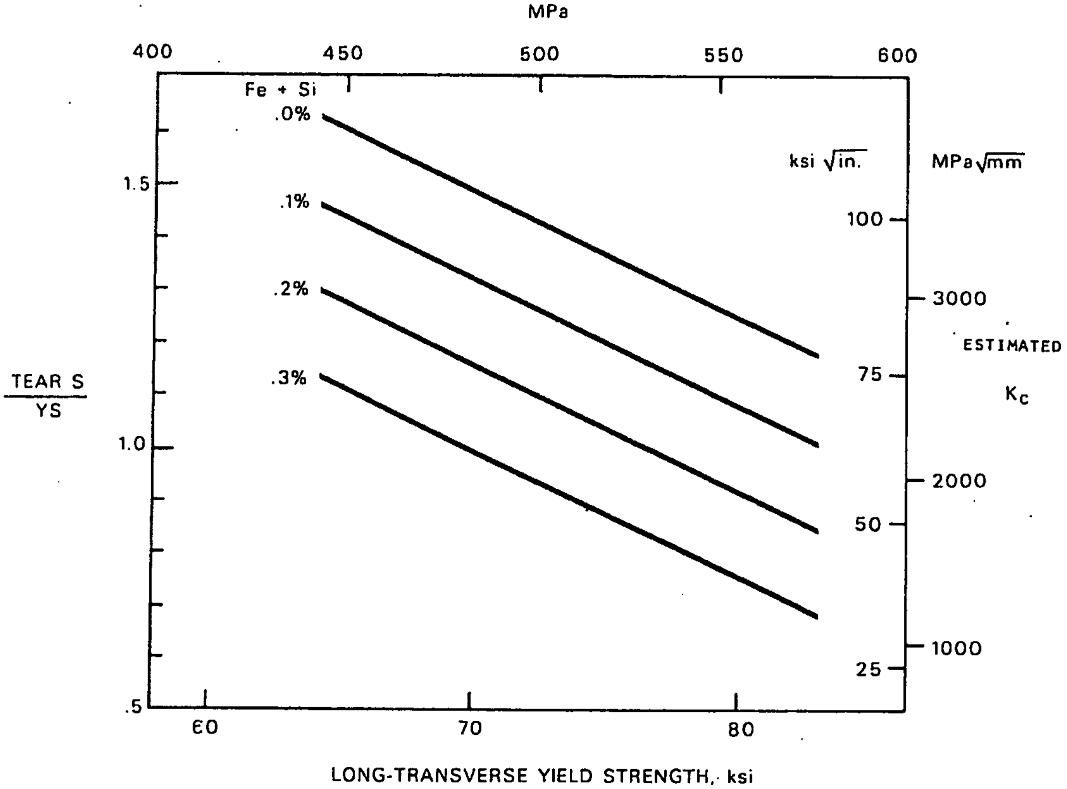


FIG. 2—*Effects of total iron plus silicon on toughness of alloy 7050 sheet.*

increased tear resistance (Fig. 3) and decreasing the volume fraction of the Al_2CuMg particles in 7050 plate increased notch toughness (Fig. 4).

Dispersoid Particles

A second class of particles called dispersoids forms by solid-state precipitation. Either chromium or manganese is added to all of the commercially established 2XXX and 7XXX alloys either to suppress recrystallization in hot worked mill products or to prevent grain coarsening in mill products cold worked prior to solution treatment. The amounts added (up to 0.3 percent chromium and 0.8 percent manganese) are retained in supersaturated solid solution during solidification but precipitate during the ingot preheat treatment as $Al_{12}Mg_2Cr$ or $Al_{20}Mn_3Cu_2$ dispersoid particles having a size of about 0.02 to 0.5 μm in the largest dimension. Once formed, these high-temperature precipitates cannot be completely dissolved, but their volume fraction, size, and distribution can be modified somewhat by thermal mechanical treatments.

Examination of fractographs of mating specimen surfaces revealed the role of $Al_{12}Mg_2Cr$ dispersoids in the fracture process (Fig. 5). One of these particles was almost invariably detected in a dimple on one or the other of the fractured surfaces. Moreover, examination of fractographs (Fig. 6) and random sections (Fig. 7) of specimens exhibiting high and low tear

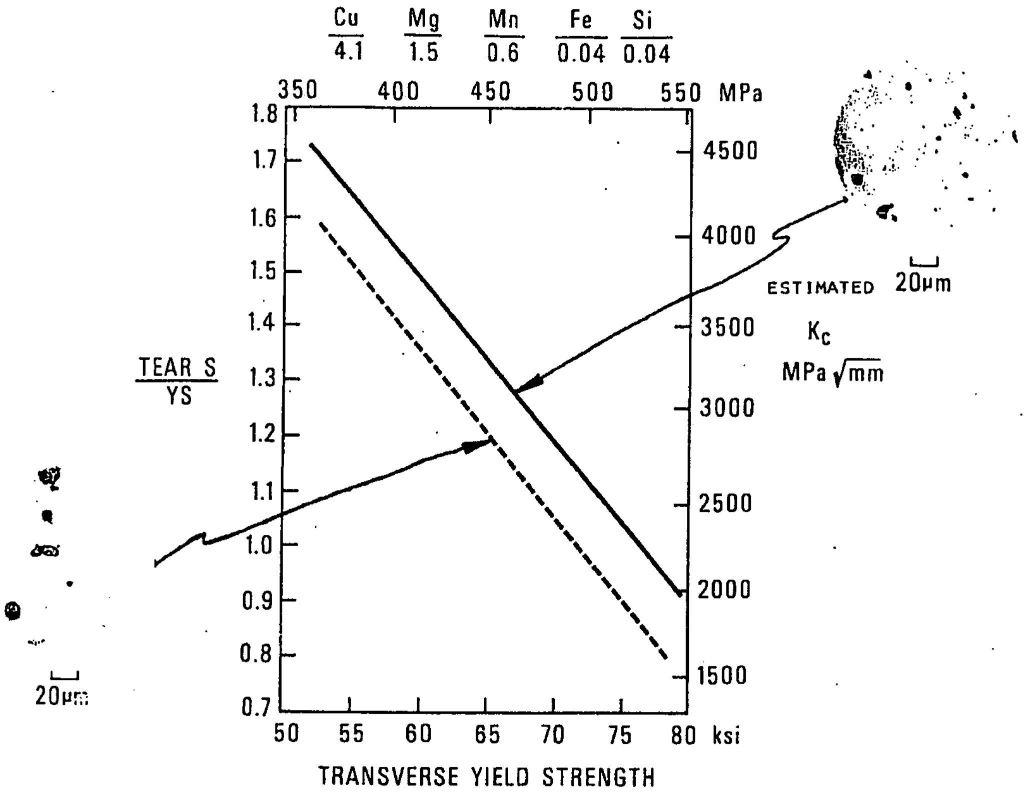


FIG. 3—*Effects of* Al_2CuMg *constituent size on the toughness of 2124 sheet.*

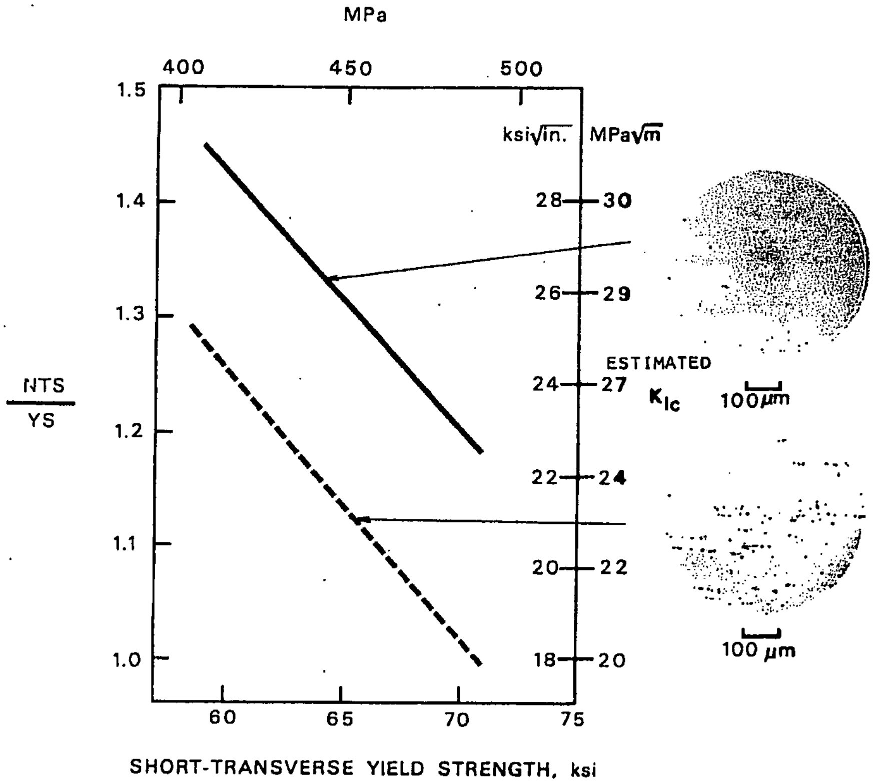


FIG. 4—*Effects of amount of* Al_2CuMg *constituent on the toughness of 7050 plate.*

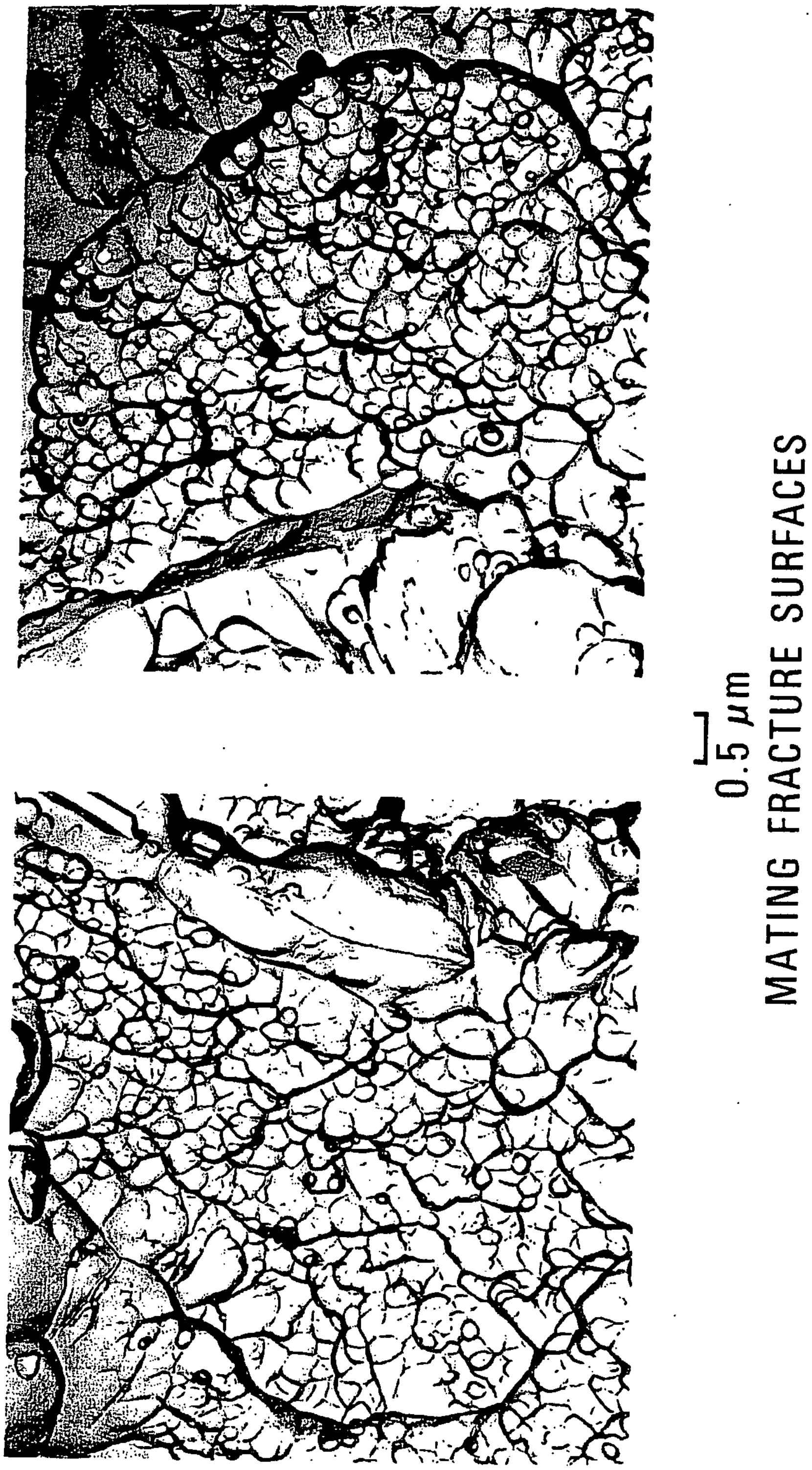
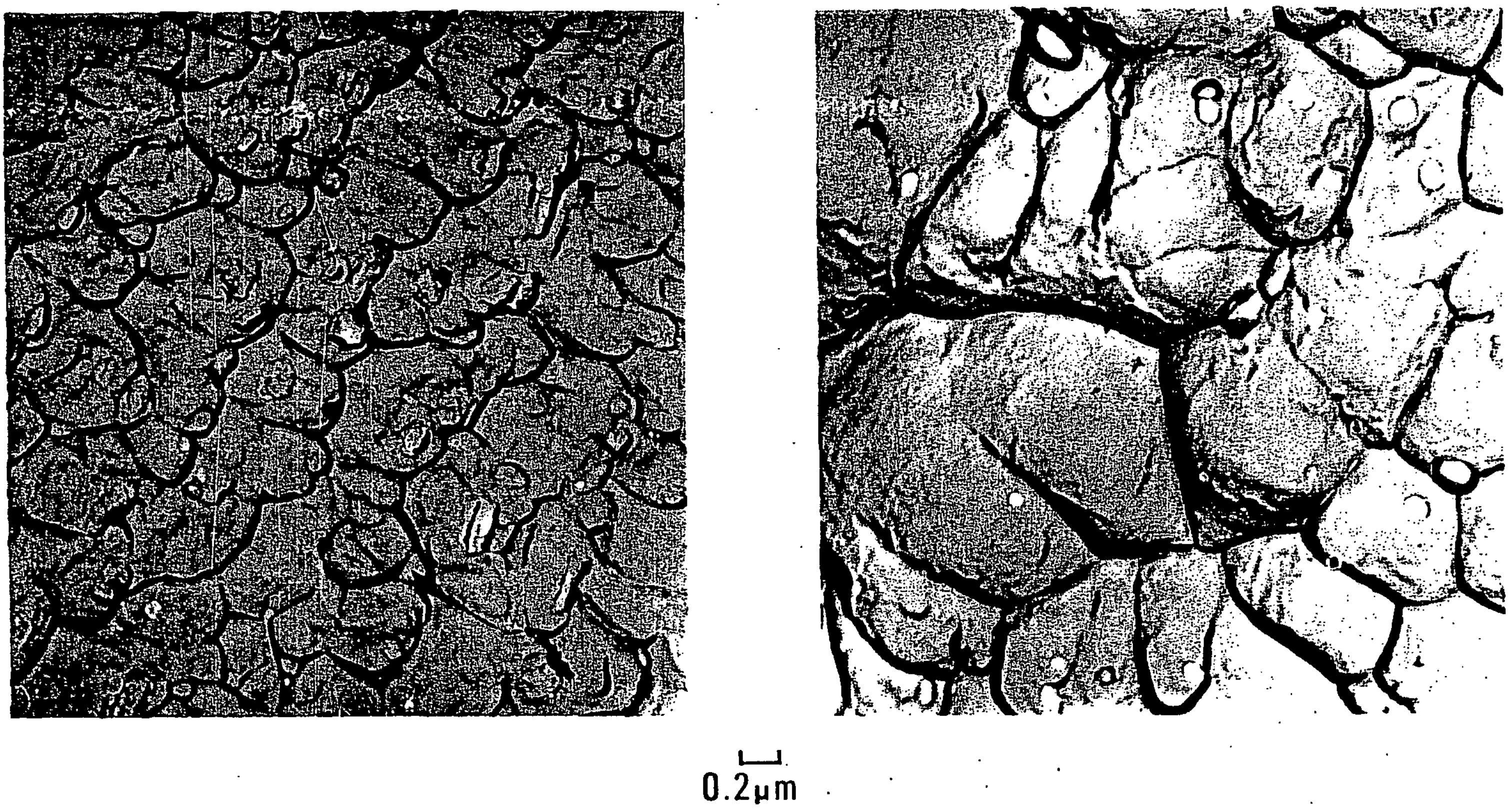
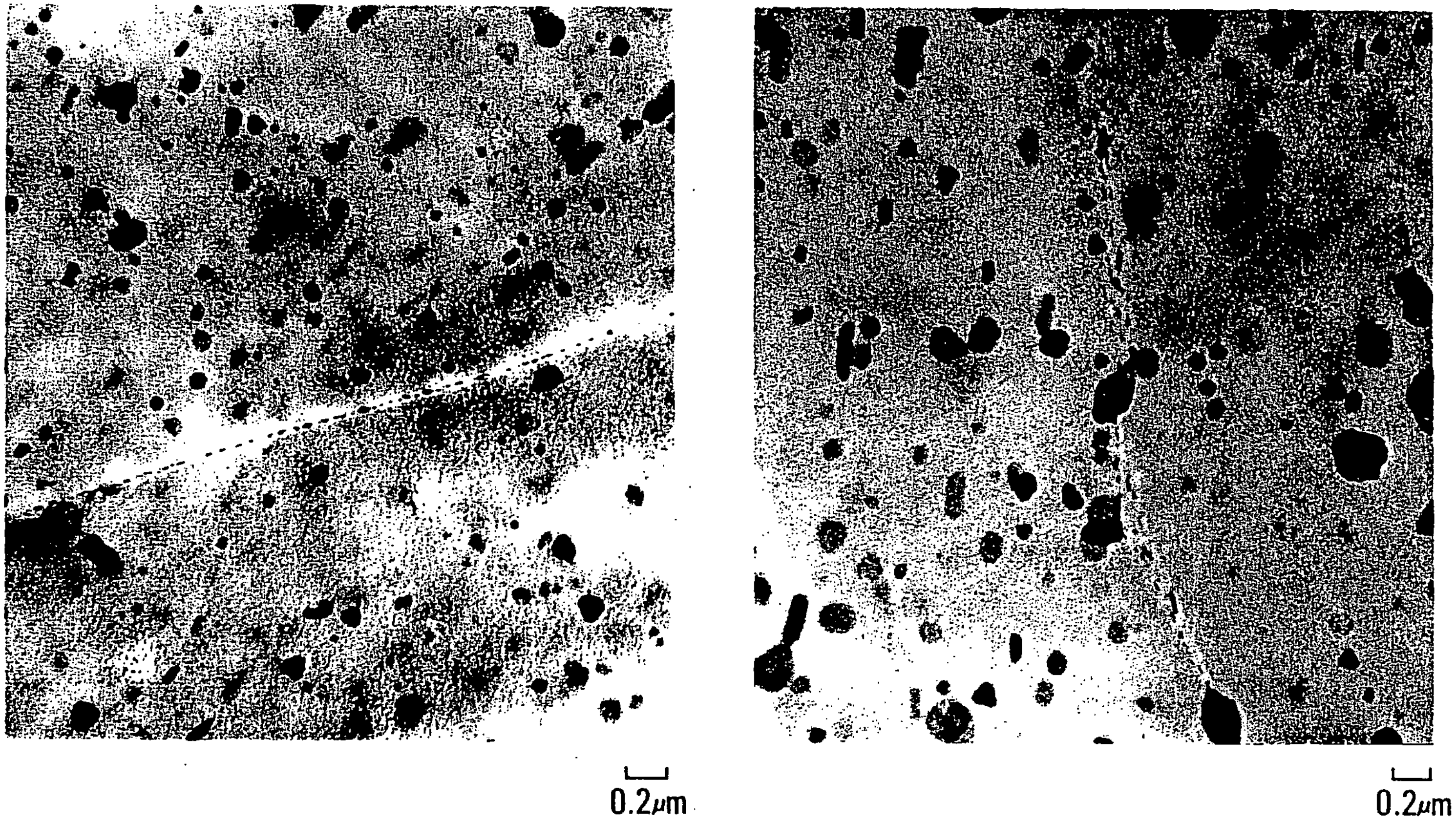


FIG. 5—*Oxide replicas of mating fractured tear specimens of 7075 sheet.*



90 in.-lb/in.^{2}	(16 Nmm/mm^2)	CRACK PROPAGATION ENERGY	470 in.-lb/in.^{2}	(82 Nmm/mm^2)
45 ksi $\sqrt{\text{in.}}$	(50 MPa $\sqrt{\text{m}}$)	ESTIMATED K_c	90 ksi $\sqrt{\text{in.}}$	(100 MPa $\sqrt{\text{m}}$)

FIG. 6—*Oxide replicas of fractured tear specimens of 7475 sheet.*



HIGH DENSITY OF $Al_{12}Mg_2Cr$ DISPERSOIDS

LOW DENSITY OF $Al_{12}Mg_2Cr$ DISPERSOIDS

FIG. 7—*Transmission electron micrographs of 7475 sheet having high- and low-areal densities of dispersoids.*

resistance indicated that toughness increased with increasing dimple size and with decreasing number of dispersoids. Quantitative metallography of fractographs of tear specimens from several lots of commercial and super purity 7075 sheet exhibiting a wide range of crack propagation energies confirmed the effect of dispersoid density (Fig. 8). Tests of experimental alloys, however, revealed that the energy to propagate a crack decreased linearly with increasing chromium content (Fig. 9). The process by which the microvoids form at dispersoids and coalesce to link fractured constituents has been termed void sheet formation [9].

Because dispersoids which contain chromium strongly affect toughness, effects of substituting either manganese or zirconium for the chromium in alloy 7475 have been examined. In one investigation, 3-in.-thick 7475 plate (0.2 percent chromium) and similar plate containing either 0.5 percent manganese or 0.1 percent zirconium were examined and tested. Structural examinations indicated differences in both dispersoids and grain structure (Fig. 10). Both tear strength : yield strength ratios and crack propagation energies indicated that substituting zirconium for chromium increased toughness and that substituting manganese for chromium decreased toughness. Subsequent K_{Ic} measurements (Table 1) using compact fracture toughness specimens from plate aged to the same strength level confirmed the harmful effects of manganese but failed to substantiate the advantage of the zirconium. These results indicate that the toughness indicator can influence relative ranking of the toughness of aluminum alloys.

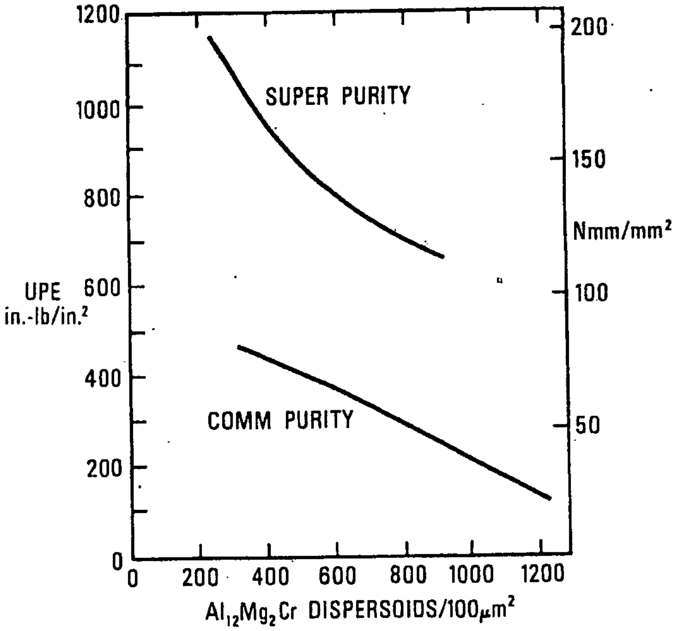


FIG. 8—*Unit crack propagation energy of 7075 sheet versus density of dispersoids on fractured surface.*

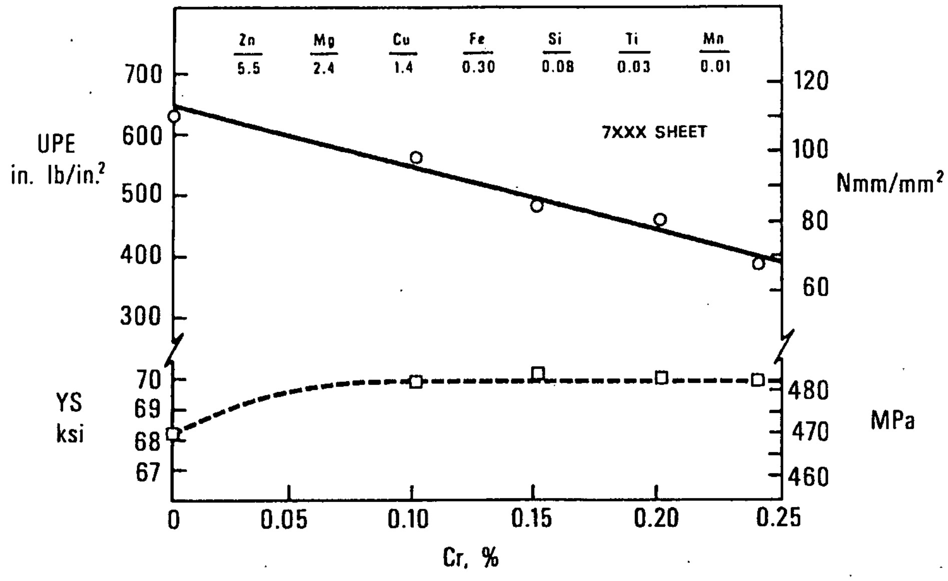


FIG. 9—*Effect of chromium content on unit crack propagation energy and yield strength.*

Comparative effects of the dispersoid-forming elements chromium, zirconium, and manganese on the toughness of super purity 7XXX alloy sheet have also been studied. In one experiment, fine grained sheets of alloys containing either 0.2 percent chromium, 0.3 percent manganese, or 0.1 percent zirconium developed comparable tear resistance. Tear resistance of the alloy containing both zirconium and chromium was on the low side of the band (Fig. 11), but the tear resistances of the alloys containing only one ancillary element appeared to be comparable.

Comparison of the test results of the plate and sheet indicates that effects of dispersoids on toughness may also be associated with their effect on grain structure.

Hardening Precipitates

A third microstructural feature in these alloys forms after the solution treatment either inadvertently during the quenching or in a controlled manner during precipitation heat treatments (aging). The size of these features ranges from about 10^{-3} μm for Guinier-Preston (G-P) zones

TABLE 1—*Effect of ancillary element addition on* K_{Ic} *of high-purity 7075-type plate.*

	Yield	Strength	K_{Ic}, ksi$\sqrt{\text{in.}}$ (MPa$\sqrt{\text{mm}}$)		
	ksi	(MPa)	0.2% Cr	0.1% Zr	0.5% Mn
L-T	65	(445)	40.2 (1400)	38.3 (1330)	33.7 (1175)
T-L	63	(430)	37.4 (1300)	32.3 (1125)	29.1 (1015)
S-L	59	(410)	28.6 (1000)	29.2 (1015)	25.0 (870)

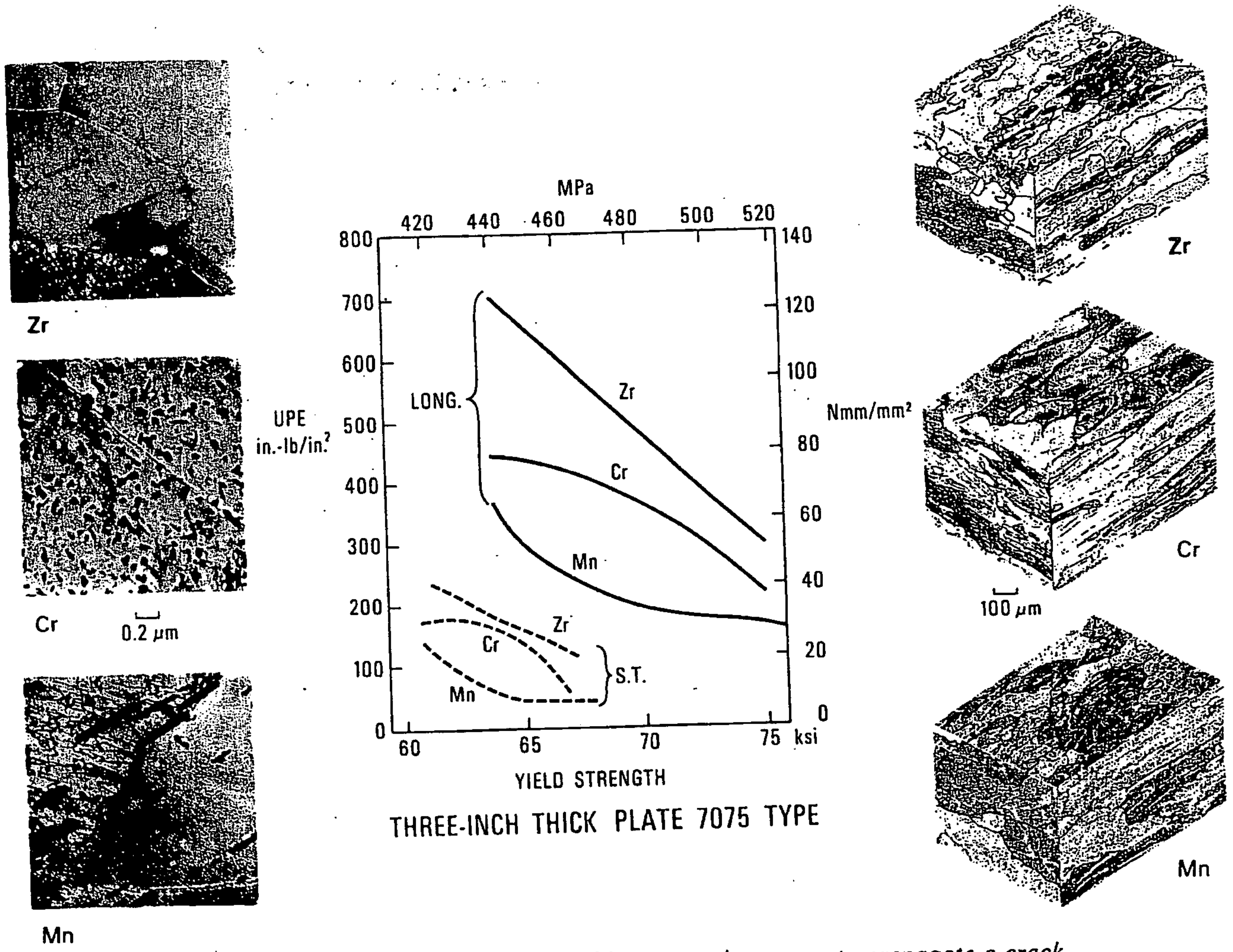


FIG. 10—*Effect of ancillary element additions on the energy to propagate a crack.*

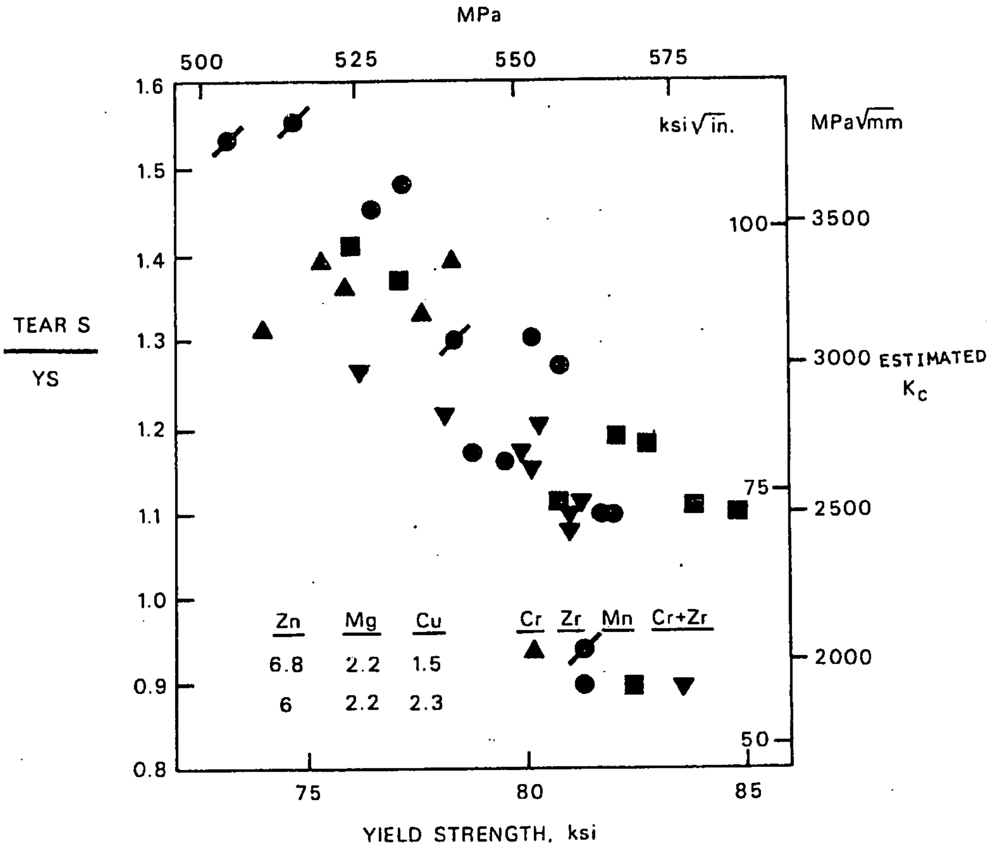


FIG. 11—*Effect of ancillary element addition on the tear strength: yield strength ratio of super purity 7XXX alloy sheet.*

formed at room temperature up to about 1 μm for coarse grain boundary precipitate formed during slow quenching or on drastic overaging.

Effects of precipitate morphology on toughness are different for the 2XXX and 7XXX alloys. Alloy 2024-T4 sheet which hardens by submicroscopic G-P zones develops higher toughness than overaged 2024 sheet which has a structure of coarse, corrugated, lath-type crystalline precipitates [*12,14*]. Cold working prior to artificial aging refines the crystalline precipitates, but underaged 2024 sheet develops higher toughness than sheet overaged to the same strength level (Fig. 12).

In contrast to these results, tear tests of five lots of 7075 and 7475 sheet indicated that intragranular precipitate morphology in alloys of this type (Fig. 13 shows test results of two lots) had no significant effect. Alloy 7075-W sheet, which age hardens by submicroscopic G-P zone precipitates, developed the same tear resistance as overaged 7075-T73 sheet which had a structure containing crystalline precipitates up to about 0.02 μm in the longest dimension (Fig. 14). The 7075-T6 sheet samples developed the highest strength and the lowest tear resistance. The hardening precipitate structure consisted of coarse G-P zones and fine crystalline precipitate.

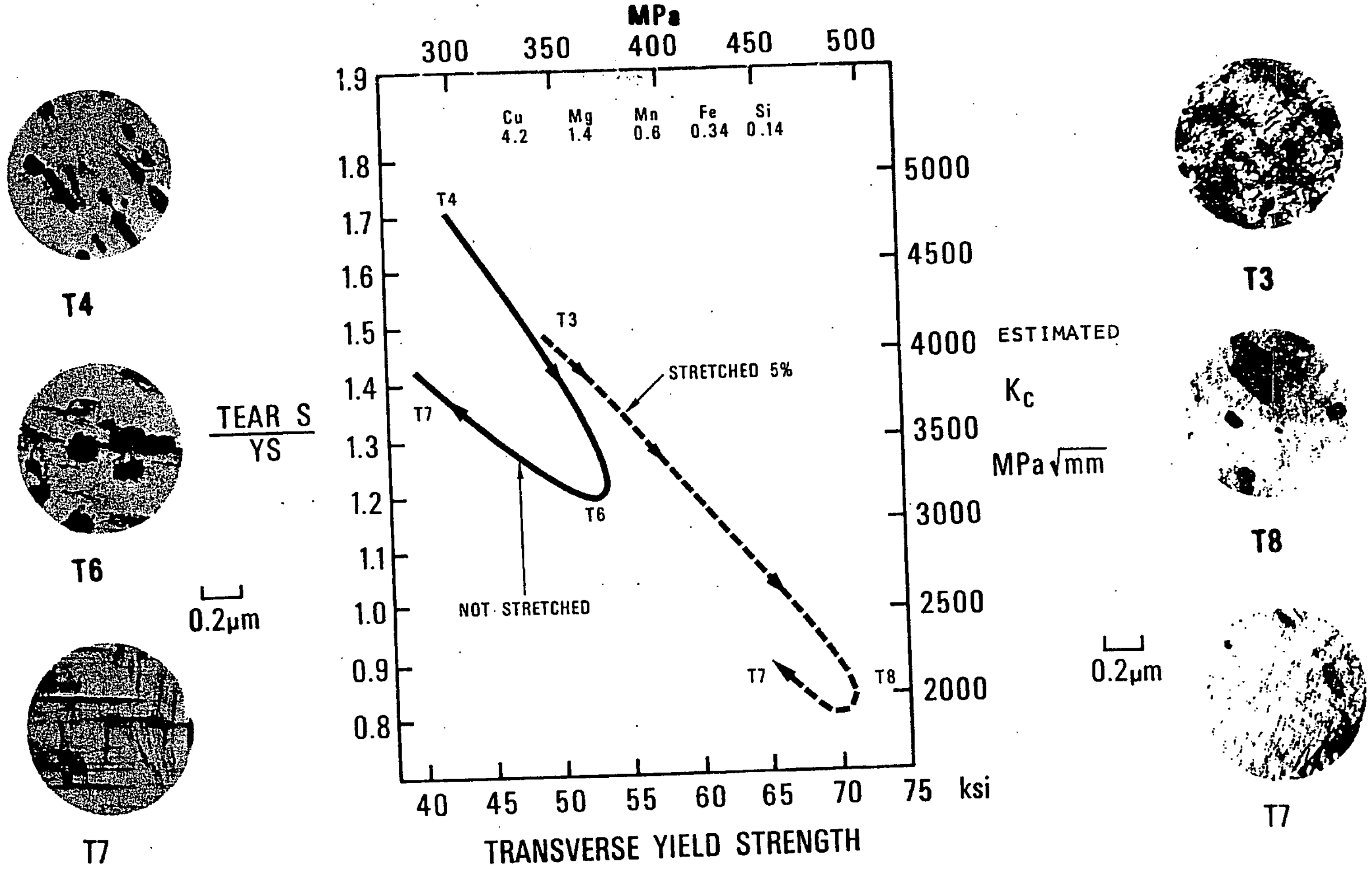


FIG. 12—*Effect of age hardening precipitate structure on the tear strength: yield strength ratio of 2024 sheet.*

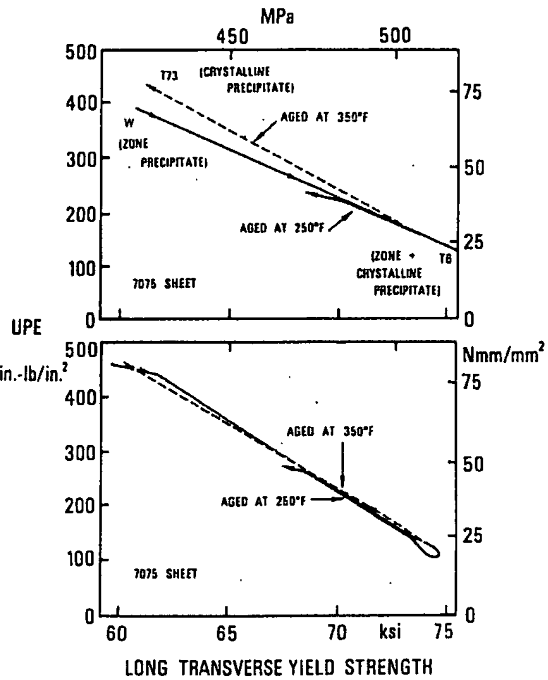


FIG. 13—*Effect of precipitation heat treatment practice on the unit crack propagation energy in 7075 sheet.*

Grain boundary precipitate, however, significantly affects toughness by controlling the relative amounts of intergranular fracture [*12,15*]. The morphology of these precipitates is affected by composition, grain structure, and quenching as well as aging conditions. High-solute contents, high-angle grain boundaries, slow quenching, and high-temperature aging treatments that are not preceded by low-temperature aging treatments may produce grain boundary precipitates and wide precipitate-free zones which favor intergranular fracture and low toughness.

Effects of differences in grain structure on the precipitate morphology and consequent effects on intergranular fracture and notch toughness are illustrated by an experiment with alloy 7050 plate. In this experiment 4.5-cm-thick plates having either almost completely unrecrystallized or almost completely recrystallized grain structures were prepared using thermal mechanical treatments. A range of yield strengths was obtained by overaging a series of samples at 325°F (436 K) following solution treatment, quenching, stretching 2 percent, and preaging 24 h at 250°F (394 K). Toughness in the transverse direction was characterized using notch tension specimens. Notch toughness of the unrecrystallized plate was higher than that of the recrystallized plate at comparable yield strengths (Fig. 15 shows results of short-transverse tests).

The relatively high toughness of the unrecrystallized material is attributed to structural features within the grains and at grain boundaries (Fig. 16). The large number of dislocations and low angle grain boundaries act

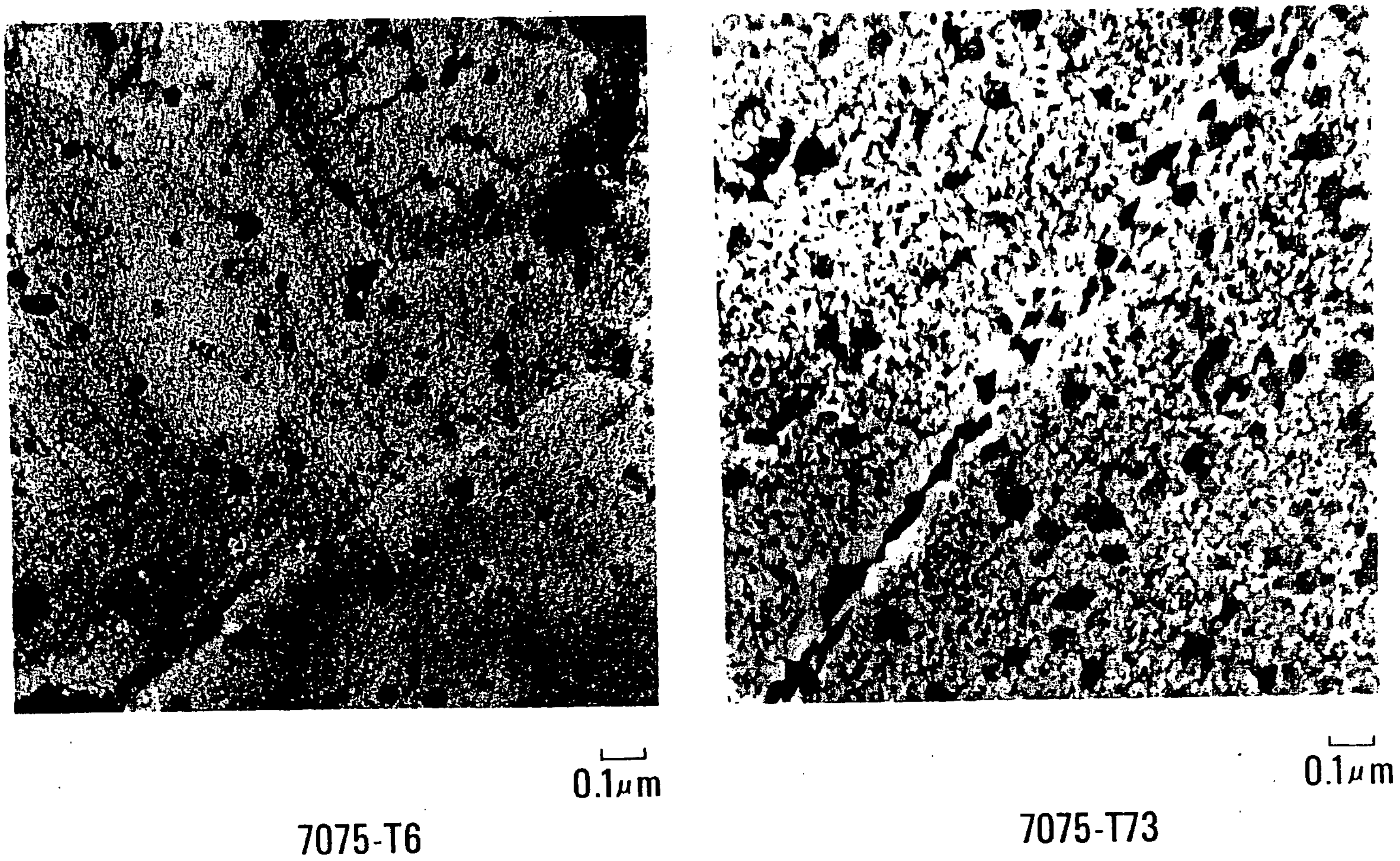


FIG. 14—*Transmission electron micrographs of 7075-T6 and 7075-T73 sheet.*

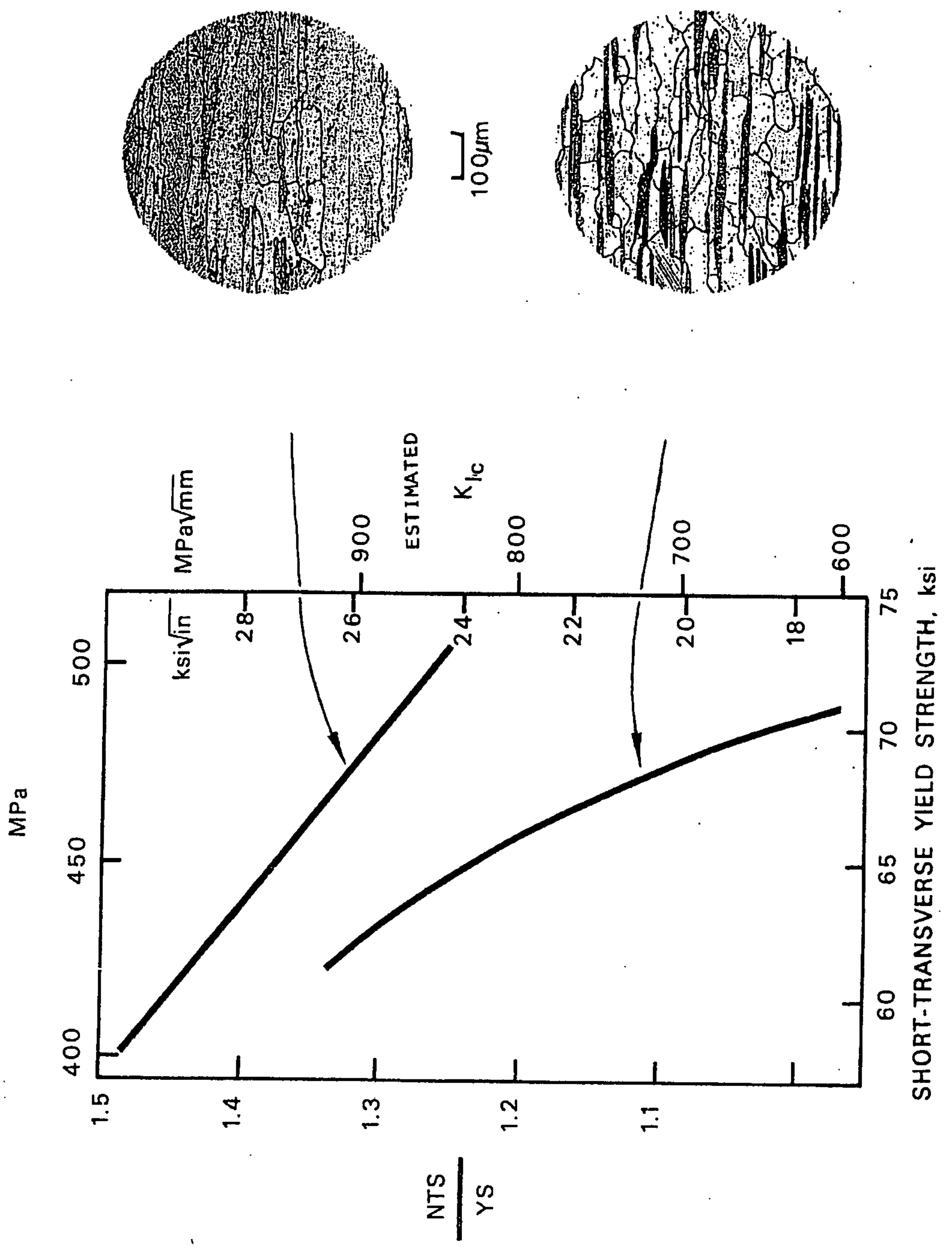
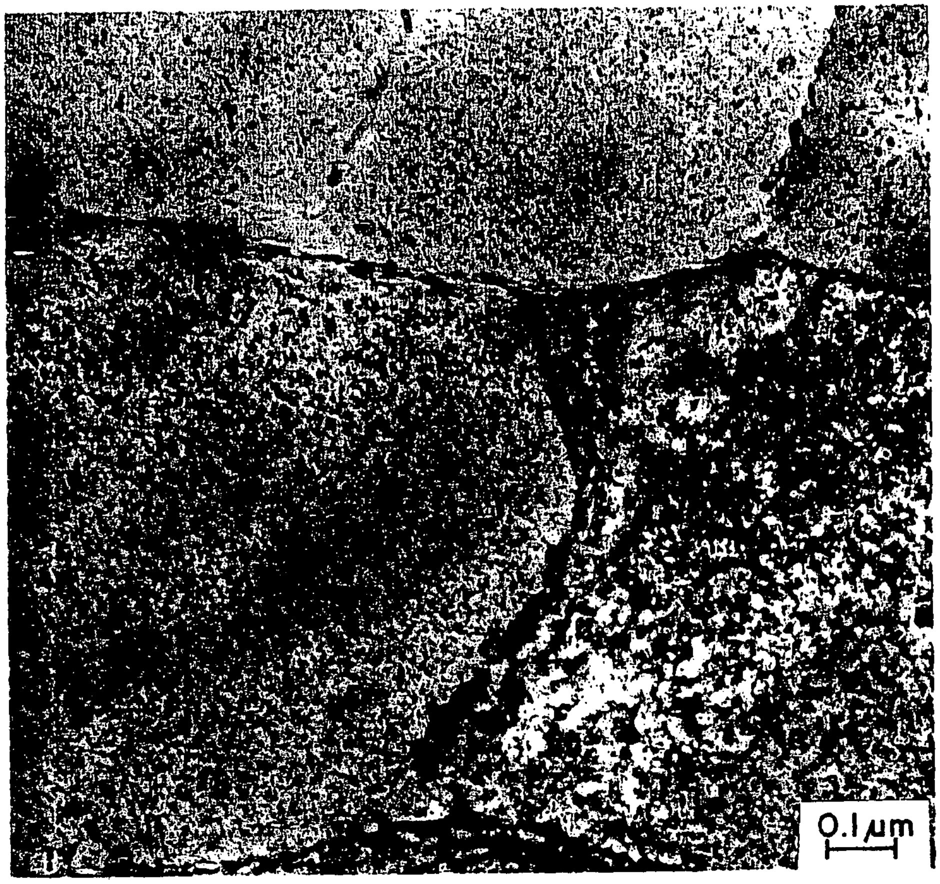


FIG. 15—*Effect of degree of recrystallization on notch toughness of 7050 plate.*

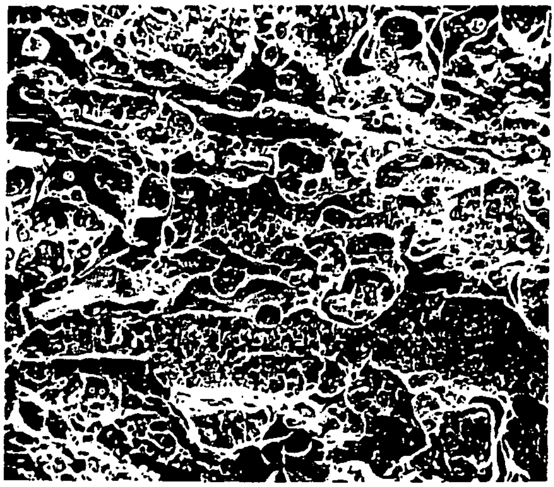


NOTE THE SUB-GRAIN STRUCTURE AND THE PLATELET MORPHOLOGY OF THE HARDENING PRECIPITATE η'.

FIG. 16—*Transmission electron micrograph of overage 7050 plate having a low degree of recrystallization.*

as sites for precipitation of fine η' platelets. These partially coherent precipitates promote homogeneous slip by forcing dislocations to bow around the precipitate particles. In addition, the growth of incipient slip bands is impeded by the subgrain boundaries and the dislocations within the grains. Consequently, dislocations cannot pile up at grain boundaries. Moreover, the copious precipitation on dislocations and low-angle boundaries precludes the formation of large, brittle grain boundary precipitates and of wide precipitate-free zones (PFZ). As a result, the material fractures largely by the transgranular dimple rupture mode (Fig. 17, top).

The lower toughness of the recrystallized plate is attributed to a larger proportion of intergranular fracture caused by alterations in the dislocation, precipitate, and grain boundary structures (Fig. 18). Because few subgrain boundaries are present, slip bands can develop the length of the grain when the recrystallized material is stressed. These dislocations pile



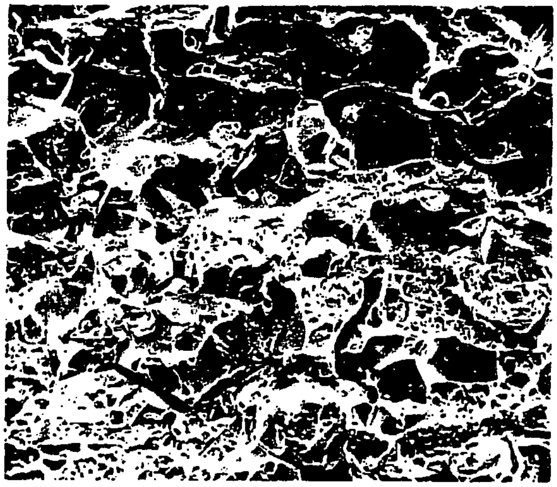
SHORT-TRANSVERSE PROPERTIES

YS 70 ksi (480 MPa)

$\frac{NTS}{YS}$ 1.22

EST K_{Ic} 24.5 ksi$\sqrt{in.}$ (860 MPa$\sqrt{mm}$)

SAMPLE NO. 418966-14B-2
ALMOST COMPLETELY UNRECRYSTALLIZED



YS 70 ksi (480 MPa)

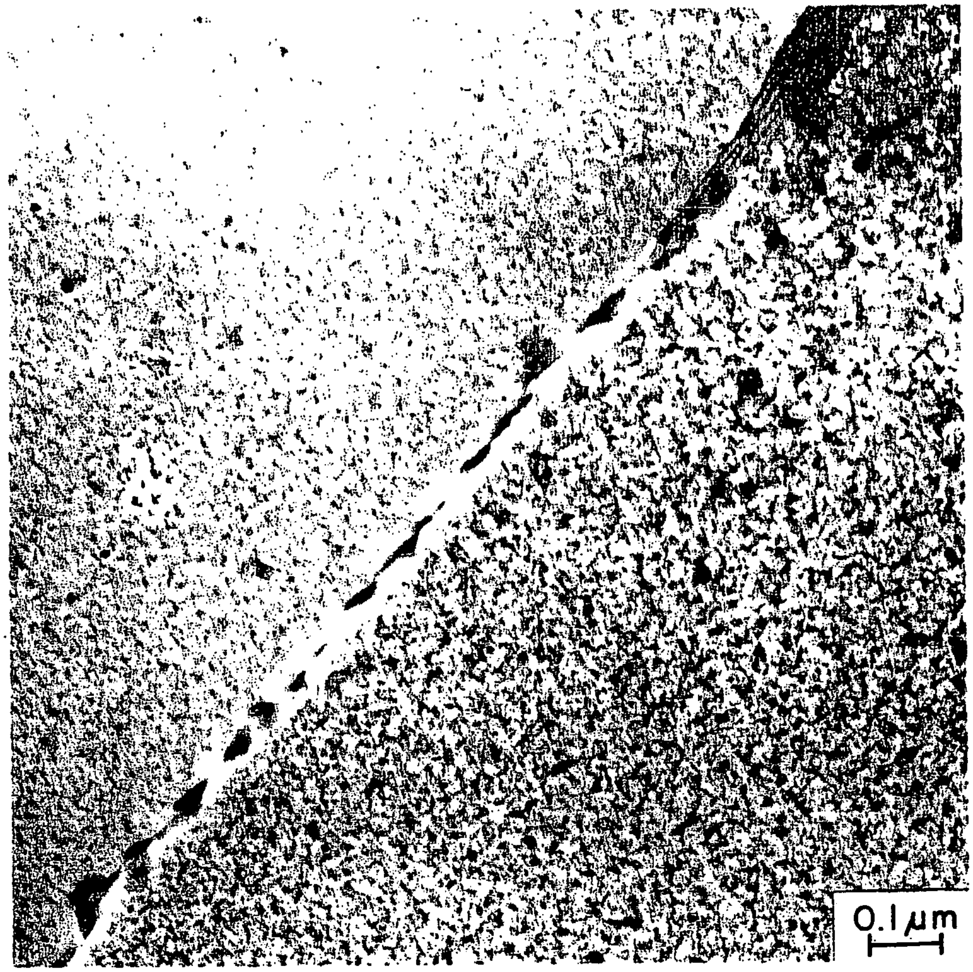
$\frac{NTS}{YS}$ 0.96

EST K_{Ic} 17 ksi$\sqrt{in.}$ (600 MPa$\sqrt{mm}$)

SAMPLE NO. 418966-34B-1
ALMOST COMPLETELY RECRYSTALLIZED

FIG. 17—*Illustrates high degree of intergranular fracture in almost completely recrystallized 7050 plate.*

up at grain boundaries and exert a force for intergranular separation. Furthermore, the high-angle boundaries act as vacancy sinks, thus promoting the development of a wide PFZ during artificial aging. Finally, the high-angle boundaries are preferred sites for nucleation of coarse equilibrium precipitates which weaken the grain boundaries. The combination of the stress exerted by the dislocations, the wide PFZ, and the



NOTE THE WIDE PFZ AND LARGE GRAIN BOUNDARY PRECIPITATES.

FIG. 18—*Transmission electron micrograph of overaged 7050 plate having a high degree of recrystallization.*

coarse grain boundary precipitates promotes fracture at or near the grain boundaries (Fig. 17, bottom).

Differences in composition which make subtle changes in hardening precipitate structure also affect toughness. Toughness of 7XXX alloys decreases with increasing magnesium content when compared at equal strength [*12*], and 7XXX alloys containing copper generally develop higher toughness than similar copper-free alloys aged to the same strength [*10*]. In general, toughness of high-solute 7XXX-T7 (overaged) products is lower than that of lower solute 7XXX-T6 (peak strength) products (Fig. 19), although toughness of individual lots is identical when compared at equal underaged and overaged strengths. The explanation for this apparent paradox is illustrated in Fig. 20. Consider a particular high-solute alloy which has high strength and low toughness. Decreasing strength by

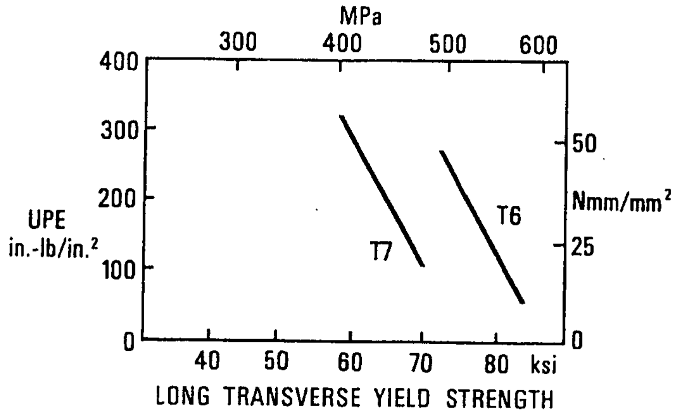


FIG. 19—*Unit crack propagation energies of commercial 7XXX alloy plate in peak strength and overaged tempers.*

modifying the aging practices increases toughness to some degree, but substituting a lower-solute alloy aged to peak strength increases toughness to a higher degree for the same sacrifice in strength.

Although cold working 2024 and most other 2XXX alloy products prior to artificial aging refines the precipitate structure and increases strength, cold working 7XXX alloy products prior to aging above about 300°F (422 K) coarsens the precipitate structure and decreases strength. This phenomenon is illustrated by the structure and properties of stretched and unstretched alloy 7050 plate which had been aged to near peak strength by

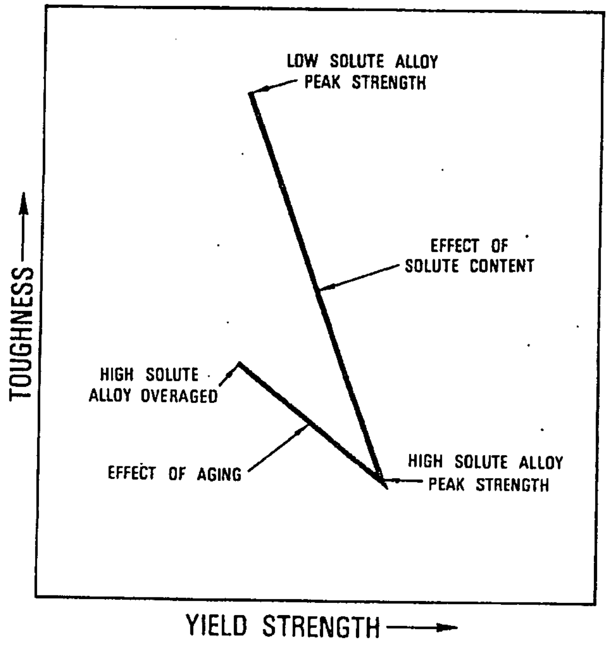
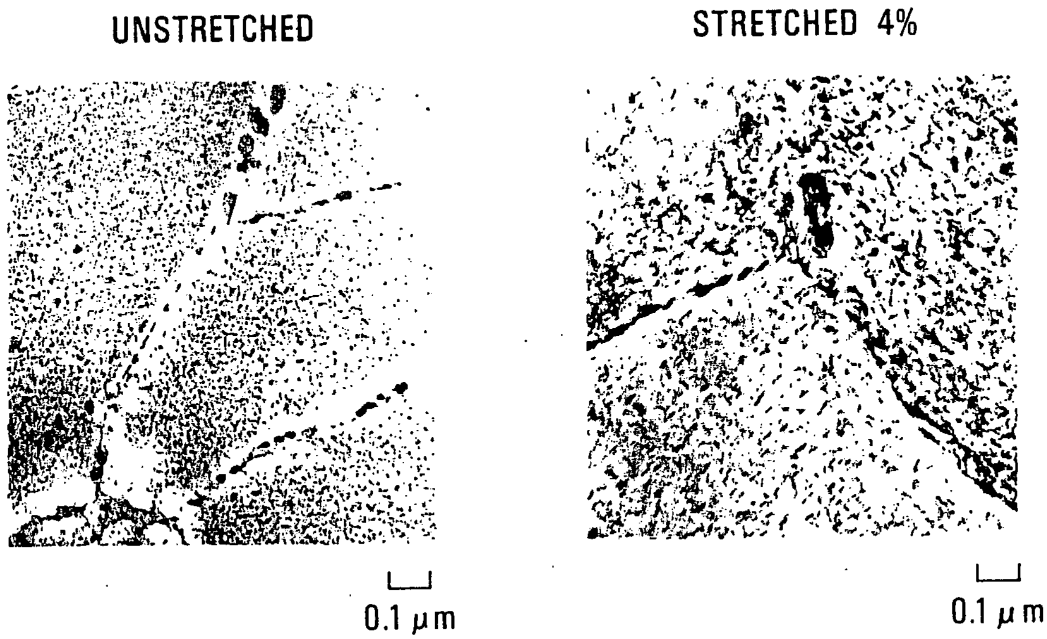


FIG. 20—*Illustrates effect of decreasing solute content and overaging on the toughness-yield strength relationship of 7XXX alloy products.*

the same practice (Fig. 21). Moreover, examinations of unstretched, overaged alloy 7050 plate and similar plate that had been stretched either 1 percent or 4 percent, then overaged to the same short-transverse yield strength, reveal that stretching progressively coarsened the precipitate structure despite the shorter aging times (Fig. 22). The notch toughness of the plate at comparable yield strengths also progressively decreased with increasing amount of stretch (Fig. 23), while the percentage of intergranular fracture increased. The change in fracture mode and decrease in toughness are attributed to alterations in deformation mechanisms within grains by the dislocations introduced during stretching.

Summary

In summary, the effects of soluble and insoluble constituents, dispersoids, and hardening precipitates on toughness of high-strength aluminum



UNSTRETCHED — YIELD STRENGTH

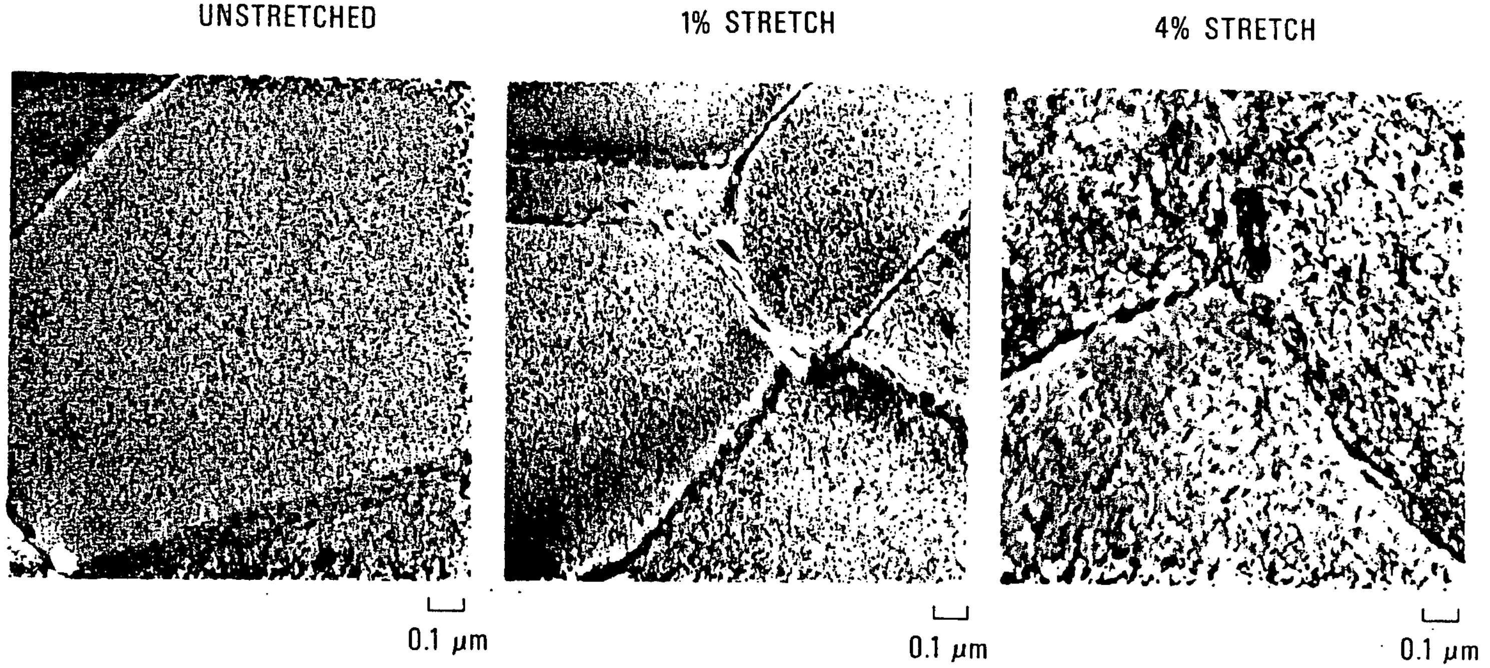
	ksi	(MPa)
L	78	(540)
LT	78	(540)
ST	77	(530)

STRETCHED 4% — YIELD STRENGTH

	ksi	(MPa)
L	74	(510)
LT	71	(490)
ST	69	(475)

ALLOY 7050 PLATE AGED 24 HOURS AT 250 F (394 K)
PLUS 14 HOURS AT 325 F (436 K)

FIG. 21—*Effects of stretching on the structure and tensile yield strength of alloy 7050 plate.*



	UNSTRETCHED	1% STRETCH	4% STRETCH
	29 HOURS AT 325°F (436 K)	20 HOURS AT 325°F (436 K)	14 HOURS AT 325°F (436 K)
YIELD STRENGTH / ksi (MPa)	70.5 (486)	70.5 (486)	69.4 (478)
NTS/YS	1.34	1.20	1.10
ESTIMATED K_{Ic} / ksi $\sqrt{in.}$ (MPa $\sqrt{mm}$)	26 (900)	23 (800)	21 (730)

FIG. 22—*Effects of stretching on the structure and short-transverse notch toughness of alloy 7050 plate aged to the same yield strength.*

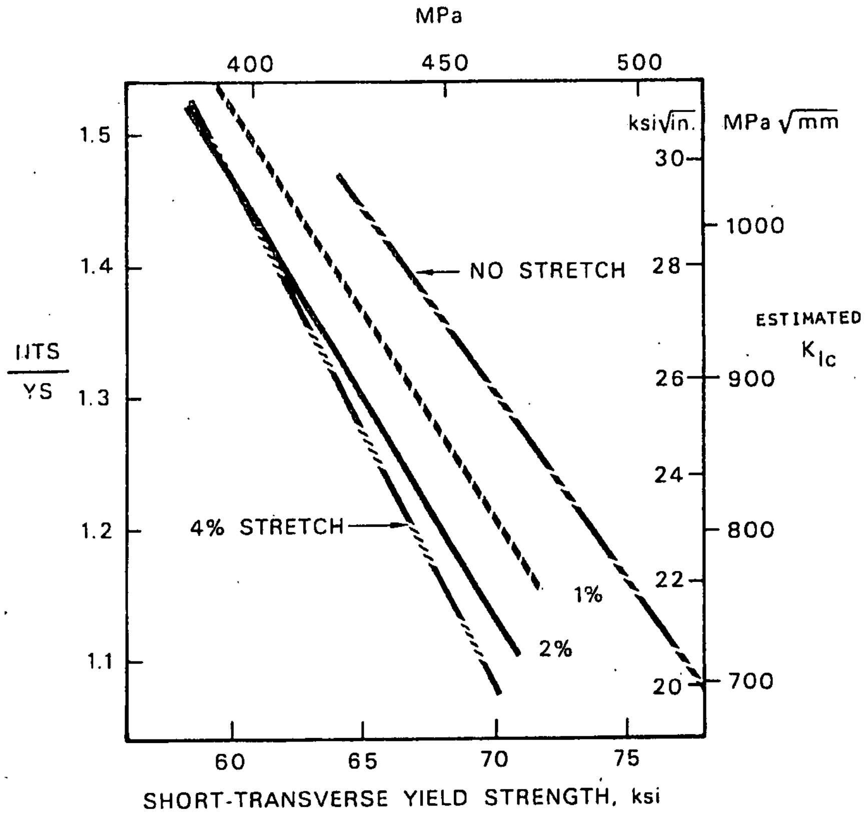


FIG. 23—*Effects of stretching on the relationship between strength and notch toughness of alloy 7050 plate.*

alloys are fairly well established. The following guidelines are offered to increase toughness by modifying these particles:

1. Minimize the volume fraction of insoluble constituents by increasing base purity.
2. Refine the size of soluble constituent particles by thermal-mechanical treatments.
3. Decrease the number of dispersoids by adjustments in chemistry or by thermal-mechanical treatments.
4. Quench as rapidly as possible.
5. Do not overage 2XXX alloy products.
6. Minimize cold work of 7XXX alloys before aging.
7. Where low residual stress is required, quench as rapidly as possible and mechanically stress relieve rather than quench slowly.
8. Age a lower-solute alloy to peak strength rather than overage a higher-solute alloy.
9. Reduce magnesium in 7XXX alloys to lowest level consistent with desired strength.
10. Where rapid quenching cannot be attained, as in plate, adjust practices to promote the lowest degree of recrystallization.

High-Toughness Alloys

New high-strength aluminum alloy products prepared according to these guidelines show promise of replacing older alloys for applications requiring high toughness with no sacrifice in strength.

Alloy 7475-T61 sheet [*14*] develops toughness approaching that of 2024-T3 at strength comparable to that of 7075-T6 sheet (Fig. 24) [*10,17,18*]. In the T761 temper, this material provides even higher toughness with strength and resistance to exfoliation corrosion comparable to that of 7075-T76 sheet. Alloy 7475-T651, T7651, and T7351 plate develop strength and corrosion resistance comparable to that of 7075 in corresponding tempers along with significantly improved toughness (Fig. 25). Because of its outstanding combination of strength and toughness, this alloy is being considered for several advanced designs and has been specified for the F-16.

Alloy 2124-T851 plate develops higher short-transverse elongation values than 2024-T851 plate along with higher fracture toughness in all directions, Fig. 26. It has seen extensive service on the F-111 and is in the F-14, F-5, B-1, and space shuttle.

Alloy 2048-T851 plate develops the toughness of alloy 2219-T851 plate at strength levels approaching those of alloy 2024-T851 plate [*19*]. It is currently being evaluated by the aerospace industry.

Other alloys contain controlled amounts of iron and silicon to provide

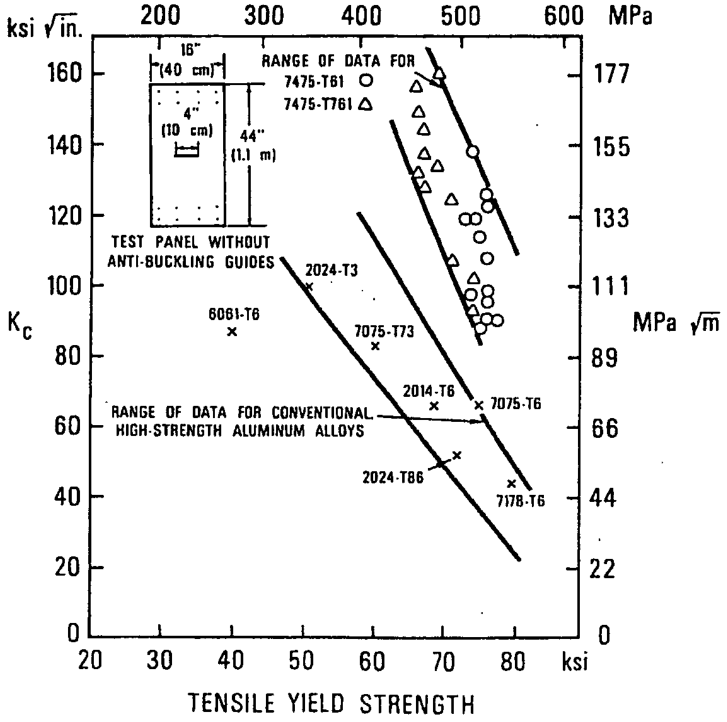


FIG. 24—K_c *of new alloy 7475 sheet relative to commercial alloy sheet.*

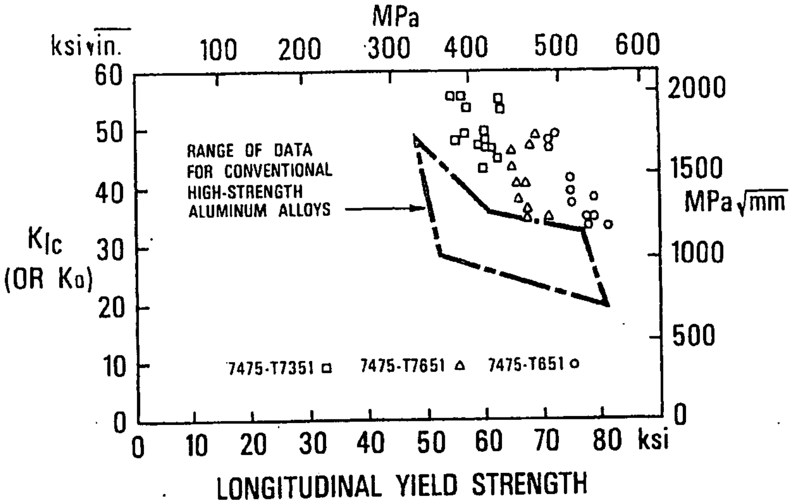


FIG. 25—K_{Ic} *of new alloy 7475 plate relative to commercial alloy plate.*

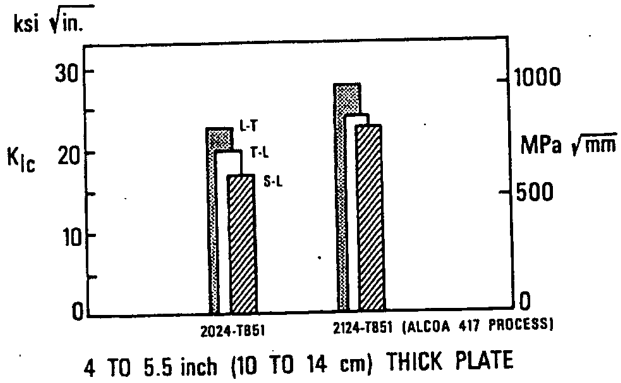


FIG. 26—K_{Ic} *of alloys 2024 and Alcoa 417 process 2124 plate.*

high toughness. Higher purity versions of alloys 2014 and 2219 which develop higher toughness than their standard purity counterparts have been evaluated. Moreover, the iron and silicon contents of alloy 7050 were established at low levels, and 7149, a higher purity version of 7049, has recently been registered with The Aluminum Association.

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DISCUSSION

W. E. Quist,[1] M. V. Hyatt,[1] and W. E. Anderson[2] (written discussion)—We would like to compliment Dr. Staley on his excellent state-of-the-art summary on the relationship between microstructure and toughness in aluminum alloys. There is one area, however, concerning the effects of the impurity elements iron and silicon on the fracture toughness of 7000-series aluminum alloys, in which we would like to add some elaboration and perhaps correction. This seems particularly relevant in that essentially all new aluminum alloys in this system have very close restrictions on iron and silicon contents, imposed almost wholly to improve their fracture toughness characteristics.

It is commonly considered that the effects of iron and silicon on fracture toughness are quantitatively similar; both causing a degrading effect.[3,4]

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[1] Research specialist, The Boeing Company, Seattle, Wash.

[2] Staff engineer, Battelle Northwest, Richland, Wash.

[3] Carman, C. M., Armiento, D. F., and Markus, H., "Plane-Strain Fracture Toughness of High-Strength Aluminum Alloys," *Transactions*, American Society of Mechanical Engineers, Dec. 1965, p. 904.

[4] Staley, J. T., this paper.

We have not found this to be the case, at least in a straight forward manner.

Effect of Iron

To our knowledge the effect of iron on the fracture toughness of 7075-7178 type alloys was discovered at Boeing in the 1961-1962 time frame.[5,6,7] Presentation (and application) of these findings was made to the Kaiser[8] and Alcoa[8] Aluminum Companies in 1961 and onward,[9] the Air Force Materials Laboratory in 1961,[10] the U. S. patent papers in 1963,[11] in the Masters thesis of W. E. Quist in 1963,[12] at the fall meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers in 1964,[13] and through the production of 60 000-70 000 lb of "low iron" 7178 for use on Boeing aircraft in 1964.[14] The principal effects that iron was found to cause in 7000-series alloys are as follows:

1. *Microstructure*—In commercial wrought 7000-series alloys, essentially all iron is found in the intermetallic phase Al_7Cu_2Fe. This massive constituent is one of the principal microstructural features in these types of alloys.[13]

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[5] It should be pointed up that for many years the general effects on intermetallic phases, oxide particles, and the like, have been recognized as being detrimental to the ductility and formability characteristics of metals, and that this had resulted in an industry movement toward vacuum melting practices and other techniques to improve the "purity" of various engineering alloys. Incidently Dr. Staley's Ref *10* (our footnote 6), which purportedly establishes Alcoa as the initial observer of the effects of iron (and silicon) on fracture toughness does not, in fact, describe these relationships. We are aware, however, of earlier unpublished work at Alcoa (1961) which was initiated in response to visits by Boeing personnel, and which did investigate the effects of iron (and other elements) on fracture toughness.

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[9] Private communications, W. E. Quist and W. E. Anderson with (1) Alcoa (H. Y. Hunsicker, J. G. Kaufman and others), 3 and 4 May 1961 and onward and (2) Kaiser Aluminum Co. (F. W. DeMoney and others), 1961 and onward.

[10] Private communication, W. E. Quist and W. E. Anderson with the Air Force Materials Laboratory, Dayton, Ohio, 1961.

[11] Anderson, W. E. and Quist, W. E., U.S. Patent No. 3,284,193, filed 5 Dec. 1963, granted 8 Nov. 1966.

[12] Quist, W. E. "Effect of Composition on the Fracture Properties of Aluminum Alloy 7178," Masters thesis University of Washington, Seattle, Wash., May 1963.

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[14] Purchase orders to Kaiser Aluminum and Reynolds Aluminum for 60000 to 70000 lb of "low iron" 7178 (other chemistry adjustments also), June 1964. Receipt of material by The Boeing Company, Seattle, Wash., began Aug. 1964.

2. *Strength*—Increased iron contents bring about an increase in the quantity of Al_7Cu_2Fe particles, and the copper contained in this constituent is unavailable for taking part in solid solution and precipitation hardening. It was independently determined that copper is not a major strengthening element in commercial 7000-series alloys, however,[13,15] and thus it is not surprising to find that iron contents up to ~ 0.50 percent do not cause major changes in yield or ultimate strengths. Examples of this behavior are shown in Fig. 27, where several alloy groups with varying iron contents are compared. (Alloys connected by solid lines have a similar chemistry except for iron.) Composition, strength, and fracture data are presented in Tables 2 and 3.

3. *Fracture Toughness*—Iron causes the fracture toughness of 7075-type alloys to decrease precipitously as iron contents are increased from 0 to 0.5 percent. See Figs. 28 and 29 for the effect of iron on several alloy compositions. It is emphasized that other composition variables (and heat treatments) were held as constant as possible in these tests, an important prerequisite to a straightforward analysis.

It recently has been suggested that a causal relationship exists between the grain size of certain of these alloys and their fracture toughness.[16] We believe this correlation is coincidental, as the grain sizes in these alloys were much too large to permit a normal Petch type fracture or strengthen-

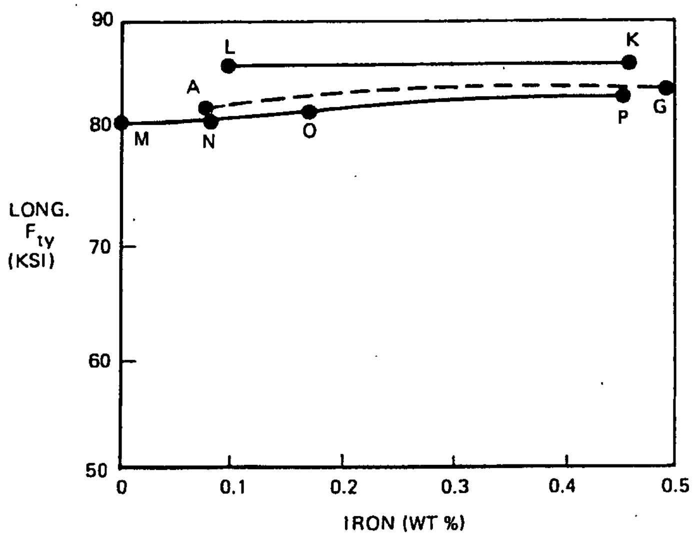

FIG. 27—*Effect of iron on yield strength (footnote 15).*

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[15] Quist, W. E. and Hyatt, M. V., "The Effect of Chemical Composition on the Fracture Properties of Al-Zn-Mg-Cu Alloys,"*Proceedings,* American Institute of Aeronautics and Astronautics American Society of Mechanical Engineers. Seventh Structures and Materials Conference, Cocoa Beach, Fla.

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TABLE 2—*Chemical compositions of several 7075-7178 type experimental alloys, weight percent (footnotes 13 and 15).*

Alloy	Cu	Fe	Si	Mn	Mg	Zn	Ni	Cr	Ti	V	Be
A	2.27	0.09	0.08	0.11	2.66	6.58	0.002	0.18	0.03	0.005	0.003
G	2.36	0.48	0.09	0.11	2.68	6.58	0.003	0.17	0.02	0.005	0.003
K	1.52	0.45	0.06	0.11	2.59	7.25	0.002	0.24	0.03	0.006	0.001
L	1.50	0.09	0.06	0.10	2.61	7.28	0.002	0.23	0.03	0.006	0.002
M	1.48	0.00	0.06	0.11	2.61	6.47	0.002	0.23	0.03	0.009	0.001
N	1.49	0.08	0.06	0.11	2.56	6.42	0.002	0.21	0.03	0.006	0.002
O	1.50	0.17	0.05	0.11	2.58	6.52	0.002	0.22	0.03	0.008	0.002
P	1.53	0.44	0.05	0.12	2.61	6.51	0.002	0.21	0.03	0.006	0.002
R	1.49	0.09	0.20	0.12	2.57	6.45	0.002	0.22	0.03	0.006	0.002
30	1.42	0.11	0.47	0.10	2.43	6.39	. . .	0.20	0.02	. . .	0.002
31	1.46	0.10	0.20	0.11	2.90	6.32	. . .	0.25	0.03	. . .	0.002

TABLE 3—*Tensile and fracture toughness properties of experimental alloy series*[a] *(footnotes 13 and 15).*

Alloy No.	Tensile[b] Strength, psi	Yield[b] Strength, psi	Elongation[b] % in 2 in.	k_c psi$\sqrt{\text{in.}}$	G_c, in-lb/in.^{2}	γ, psi/s
A	90 100	82 200	15	45 800	202	1.2×10^5
				45 662	200	1.6×10^5
G	92 000	84 000	13	38 320	141	1.4×10^5
				34 385	114	1.2×10^5
				39 242	148	1.2×10^5
				37 381	141	6.1×10^4
K	92 500	86 500	12	31 159	93	6.4×10^4
				31 195	94	6.5×10^4
L	92 100	86 200	13	47 023	213	5.6×10^4
				41 369	166	6.0×10^4
M	87 500	81 100	13	57 959	323	5.5×10^4
				60 050	347	5.6×10^4
N	88 800	81 700	13	53 173	272	5.6×10^4
				52 978	270	6.1×10^4
O	89 500	83 100	11	48 777	229	5.7×10^4
				46 261	206	5.6×10^4
P	90 300	84 100	11	40 429	157	7.6×10^4
				40 482	158	2.3×10^5
R	85 800	78 900	14	60 636	353	3.5×10^4
				61 061	358	8.0×10^3
30	76 400	69 300	13	66 400	427	3.0×10^5
				68 400	453	2.9×10^5
31	87 800	81 600	12.5	40 800	162	2.8×10^5
				45 400	200	2.8×10^5

[a] Longitudinal grain direction for 0.16-in.-thick sheet.

[b] Average value of at least two separate determinations.

[c] All data taken from center cracked panels.

$$K_c = \sigma_g \left[W \tan \frac{\pi}{W} \left(a + \frac{k_c^2}{2\pi\sigma_{ys}^2} \right) \right]^{1/2} \quad \text{(graphical solution)}$$

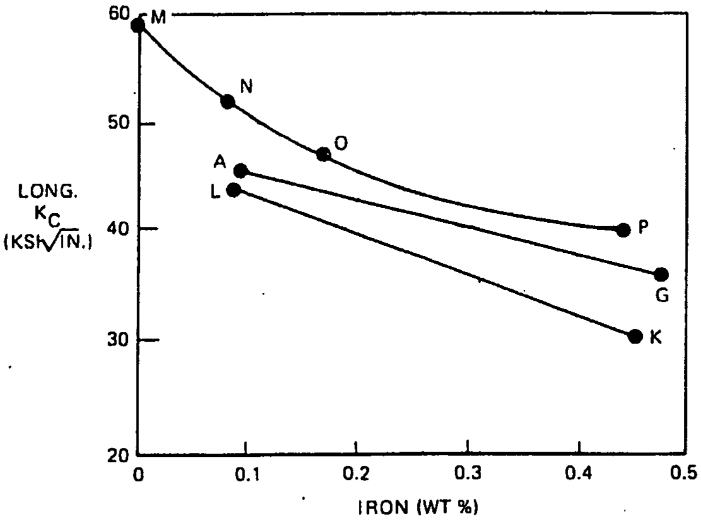

FIG. 28—*Effect of iron on toughness (footnote 15).*

ing mechanism to be operative. Furthermore, fracture paths in our alloys were completely transgranular, unlike those studied in footnote 16.

Effect of Silicon

We have found the effect of silicon on fracture toughness to be much different than that of iron, a point that did not become clear to us until 1966,[15] and which as yet has not become fully appreciated.[4] A summary of the effects of silicon on microstructure, strength, and fracture toughness are as follows:

1. *Microstructure*—In 7000-series alloys, silicon combines principally with aluminum, iron, and magnesium to form the massive silicon-bearing intermetallic compounds αAlFeSi and Mg_2Si, primarily the latter. The

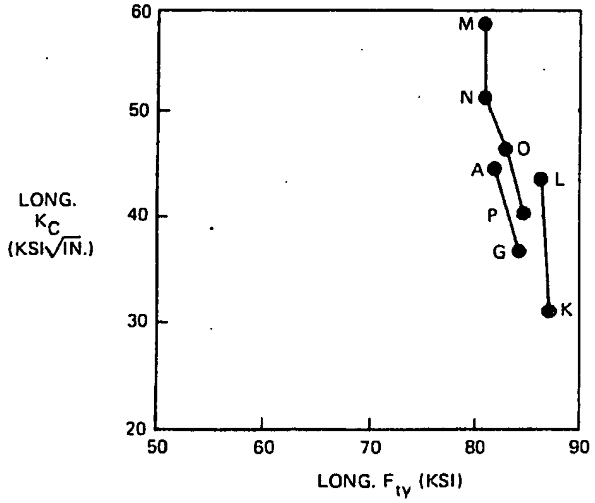

FIG. 29—*Effect of iron on toughness and yield strength (footnote 15).*

solution treating temperatures normally used for alloys in this system do not put the Mg_2Si phase into solution, and it remains as massive intermetallic particles randomly distributed throughout the microstructure.

2. *Strength*—In the Mg_2Si phase, the weight ratio of magnesium to silicon is ~1.73 to 1; thus, the presence of this phase prevents substantial quantities of the powerful strengthening element magnesium from performing its normal role in precipitation hardening. This causes a substantial decrease in both yield and ultimate strength. An example of this behavior is shown in Fig. 30 for experimental alloys *N*, *R*, and 30 where yield strength decreased from 81.7 to 69.3 ksi as silicon increased from 0.06 to 0.47 percent. See Tables 2 and 3 for composition, strength, and fracture data.

3. *Fracture Toughness*—Because of the observed formation of massive particles of αAlFeSi and Mg_2Si in the microstructure of 7000-series alloys as silicon is added, it has long been presumed by most observers that the effect of silicon on fracture toughness was degrading, similar to the effect of iron.[3,4] However, our studies did not confirm this assumption[13,15] and, in fact, showed a significant fracture toughness improvement as silicon was added. This behavior is illustrated by alloys *N*, *R*, and 30 in Fig. 31 where K_c increased from 53.1 to 67.4 ksi$\sqrt{\text{in.}}$ as silicon was increased from 0.06 to 0.47 percent. This result is somewhat understandable, since the toughness increase is accompanied by the just noted decrease in yield strength. The decreased strength is fully explainable by the formation of Mg_2Si particles, and the commensurate decrease in magnesium available for participation in hardening reactions.

In order to test whether Mg_2Si particles are inherently detrimental to toughness, independent of yield strength changes, a high silicon content

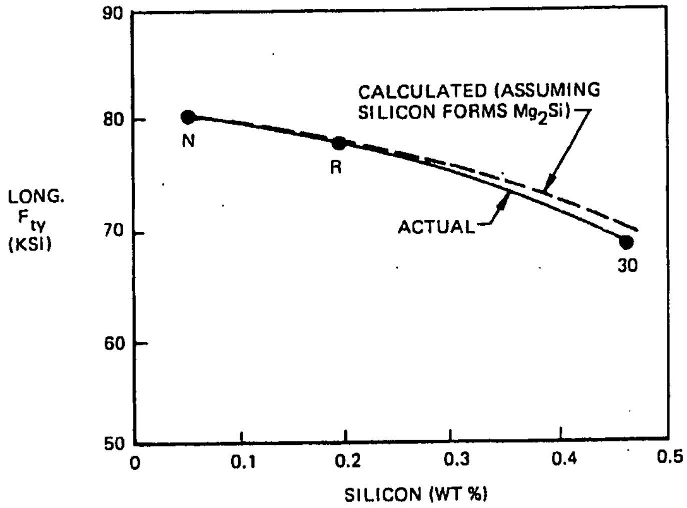

FIG. 30—*Effect of silicon on yield strength (footnote 15).*

TABLE 4—*Effect of Mg_2Si on fracture toughness (footnote 15).*

Alloy No.	Chemical Content, weight %							E_{ty}, psi	F_{tu}, psi	Elongation, % in 2 in.	K_c, psi$\sqrt{in.}$	G_c, in-lb/in.^{2}
	Zn	Mg	Cu	Fe	Si	Mn	Cr					
N	6.52	2.56	1.49	0.08	0.06	0.11	0.21	81 700	88 800	13.0	53,100	274
31	6.32	2.90	1.46	0.10	0.20	0.11	0.25	81 640	87 800	12.5	43,000	185

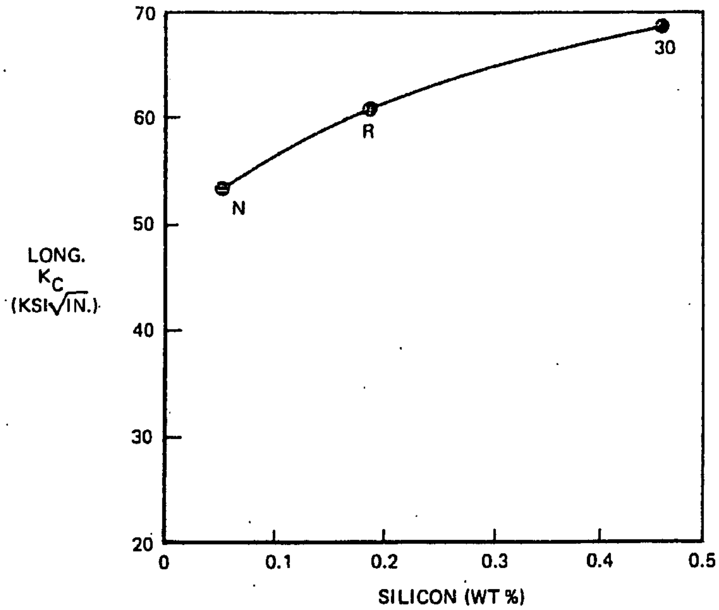

FIG. 31—*Effect of silicon on toughness (footnote 15).*

alloy was formulated (alloy 31) such that its yield strength was equivalent to a similar low silicon content alloy (alloy *N*). This was accomplished in alloy 31, by adding on extra amount of magnesium equivalent to that removed by its excess Mg_2Si particles.[15] The results are shown in Table 4. The fracture toughness of the high silicon content alloy is 43.0 ksi$\sqrt{in.}$ compared to 53.1 ksi$\sqrt{in.}$ for the low silicon content alloy, thereby demonstrating that the massive silicon bearing intermetallic particles are indeed detrimental.

From the preceding observations one deduces that the effect of lowering the iron content in established 7000-series commercial alloys will be to improve fracture toughness in a straightforward manner. For silicon content reductions, if a fracture toughness advantage is to be gained, and indeed it can be, then the nominal magnesium content of the alloy must be adjusted downward such that typical or average yield strengths are held constant. If this is not done the effect of reducing silicon content will be to increase yield strength and lower fracture toughness. For new alloys, a reduction of iron and silicon contents will bring straightforward advantages, as delta-yield-strength changes between an "old" and "new" alloy will not be a consideration.

It is hoped that these observations will clarify the important effects of iron and silicon on the fracture toughness of 7000-series alloys, at least to the extent that out studies have shown.

US005455003A

United States Patent [19]

Pickens et al.

[11] **Patent Number: 5,455,003**

[45] **Date of Patent: * Oct. 3, 1995**

[54] **AL-CU-LI ALLOYS WITH IMPROVED CRYOGENIC FRACTURE TOUGHNESS**

[75] Inventors: **Joseph R. Pickens**, Glenelg, Md.; **William T. Tack**, Littleton, Colo.

[73] Assignee: **Martin Marietta Corporation**, Bethesda, Md.

[*] Notice: The portion of the term of this patent subsequent to Nov. 9, 2010 has been disclaimed.

[21] Appl. No.: **103,662**

[22] Filed: **Aug. 10, 1993**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 32,158, Mar. 12, 1993, abandoned, which is a continuation of Ser. No. 493,255, Mar. 14, 1990, abandoned, which is a continuation-in-part of Ser. No. 327,666, Mar. 23, 1989, Pat. No. 5,259,897, which is a continuation-in-part of Ser. No. 233,705, Aug. 18, 1988, abandoned.

[51] **Int. Cl.^{6}** **C22C 21/12**

[52] **U.S. Cl.** **420/529**; 148/695; 148/698; 148/699; 148/700; 148/701; 148/416; 148/417; 148/418; 148/438; 148/439; 420/531; 420/532; 420/533; 420/539; 420/540; 420/541; 420/542; 420/543; 420/545; 420/552; 420/553

[58] **Field of Search** 420/529, 531, 420/532, 533, 539, 540, 541, 542, 543, 545, 552, 553; 148/695, 698, 699, 700, 701, 416, 417, 418, 438, 439

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Primary Examiner—David A. Simmons

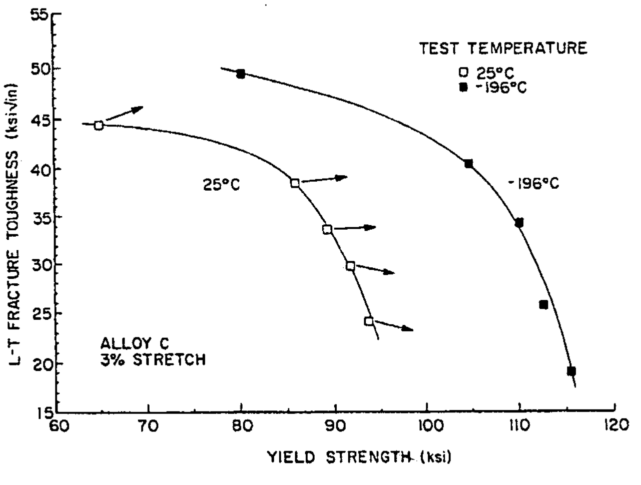
Assistant Examiner—Robert R. Koehler

Attorney, Agent, or Firm—Gay Chin; Alan G. Towner; Brian J. Rees

[57] **ABSTRACT**

A method is disclosed for the production of aluminum-copper-lithium alloys that exhibit improved strength and fracture toughness at cryogenic temperatures. Improved cryogenic properties are achieved by controlling the composition of the alloy, along with processing parameters such as the amount of cold-work and artificial aging. The ability to attain substantially equal or greater strength and fracture toughness at cryogenic temperature in comparison to room temperature allows for use of the alloys in cryogenic tanks for space launch vehicles and the like.

39 Claims, 7 Drawing Sheets



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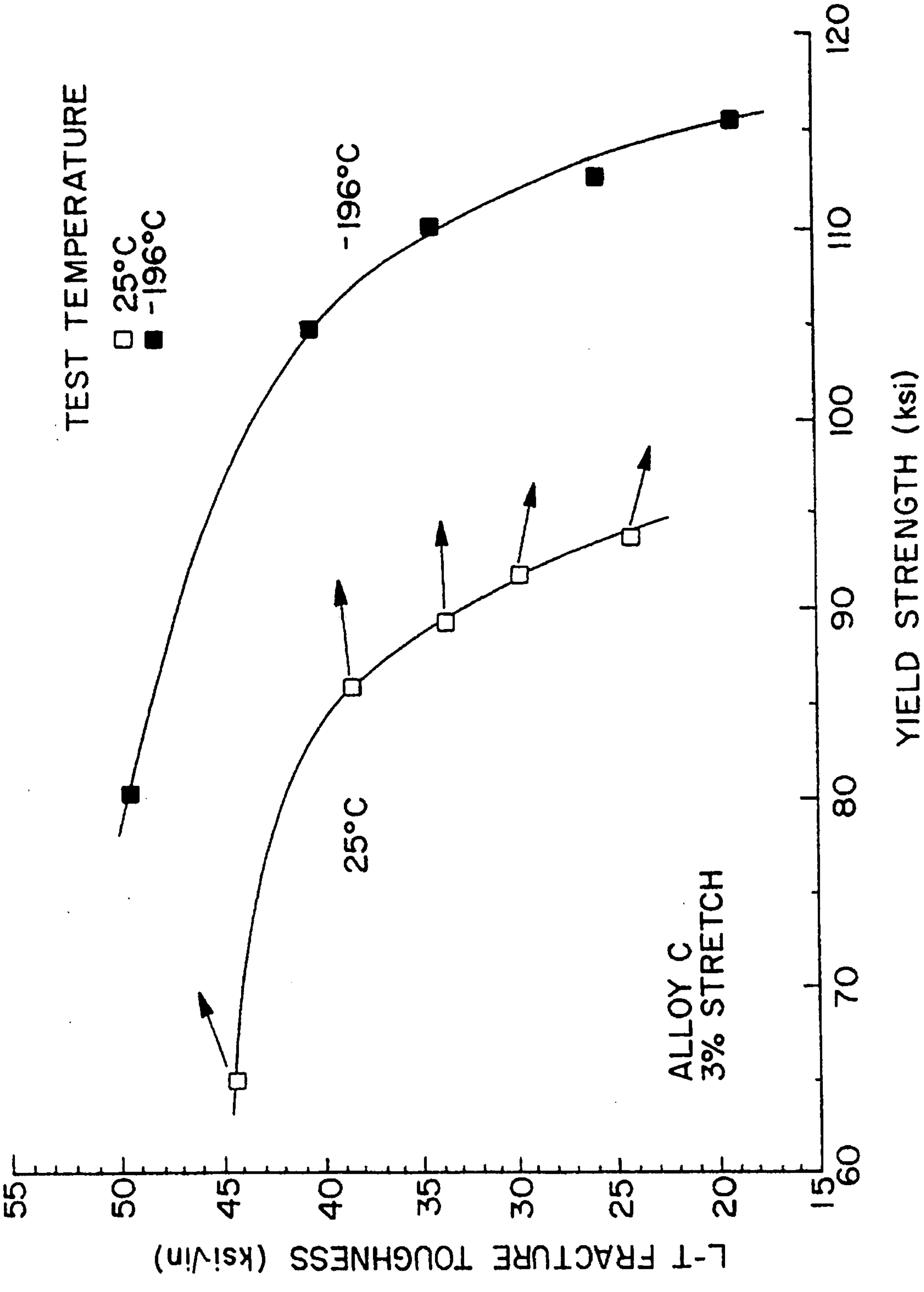
TEST TEMPERATURE
□ 25°C
■ -196°C
-196°C
25°C
ALLOY C
3% STRETCH
L-T FRACTURE TOUGHNESS (ksi√in)
55
50
45
40
35
30
25
20
15
YIELD STRENGTH (ksi)
60
70
80
90
100
110
120

FIG. 1

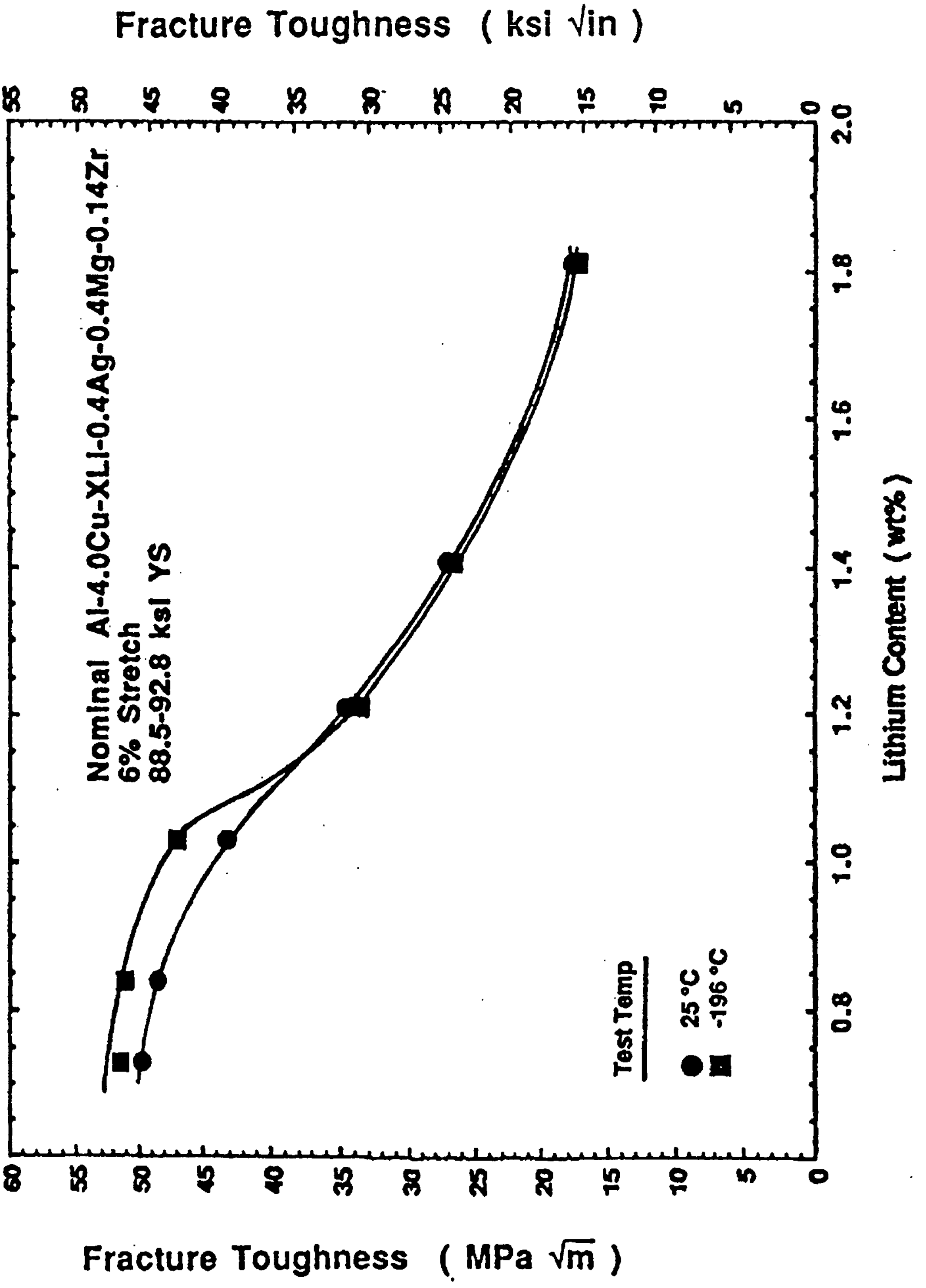
Fracture Toughness (ksi √in)
55
50
45
40
35
30
25
20
15
10
5
0
Nominal Al-4.0Cu-XLi-0.4Ag-0.4Mg-0.14Zr
6% Stretch
88.5-92.8 ksi YS
Test Temp
● 25 °C
■ -196 °C
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Lithium Content (wt%)
60
55
50
45
40
35
30
25
20
15
10
5
0
Fracture Toughness (MPa √m)

FIG. 2

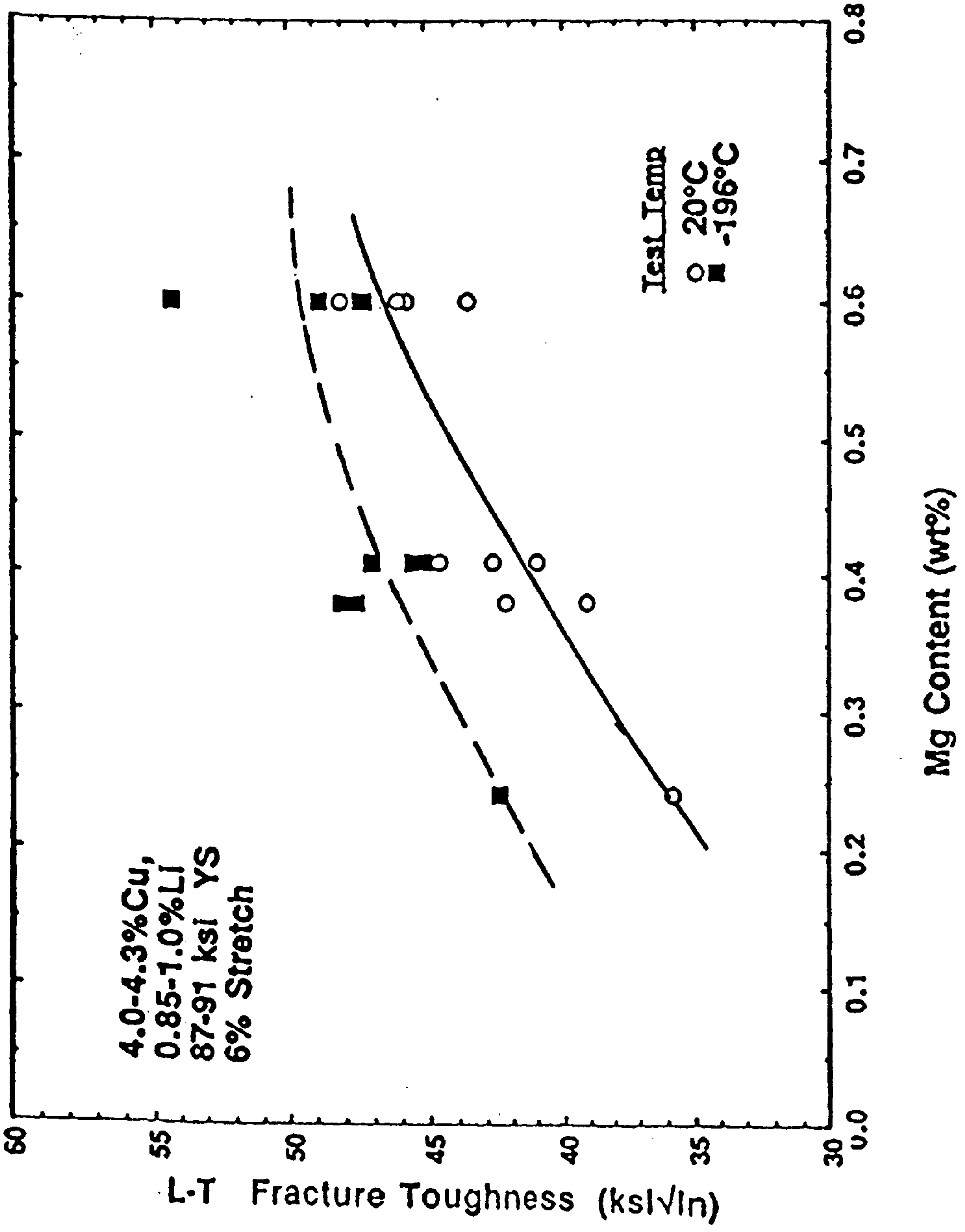
4.0-4.3%Cu,
0.85-1.0%Li
87-91 ksi YS
6% Stretch
Test Temp
○ 20°C
■ -196°C
L-T Fracture Toughness (ksi√in)
60
55
50
45
40
35
30
Mg Content (wt%)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

FIG. 3

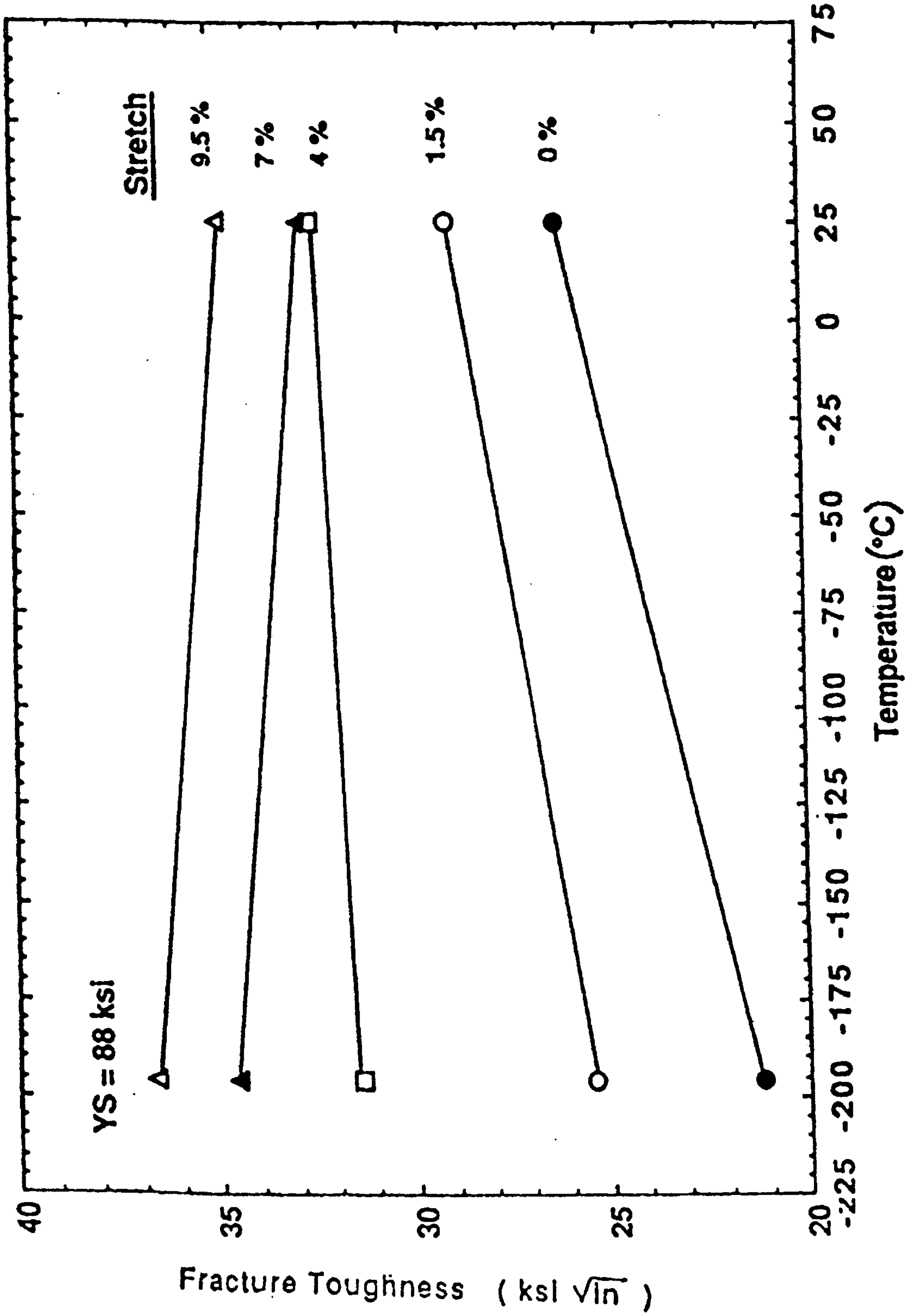
Stretch
9.5 %
7 %
4 %
1.5 %
0 %
YS = 88 ksi
Fracture Toughness (ksi √in)
40
35
30
25
20
Temperature (°C)
-225
-200
-175
-150
-125
-100
-75
-50
-25
0
25
50
75

FIG. 4

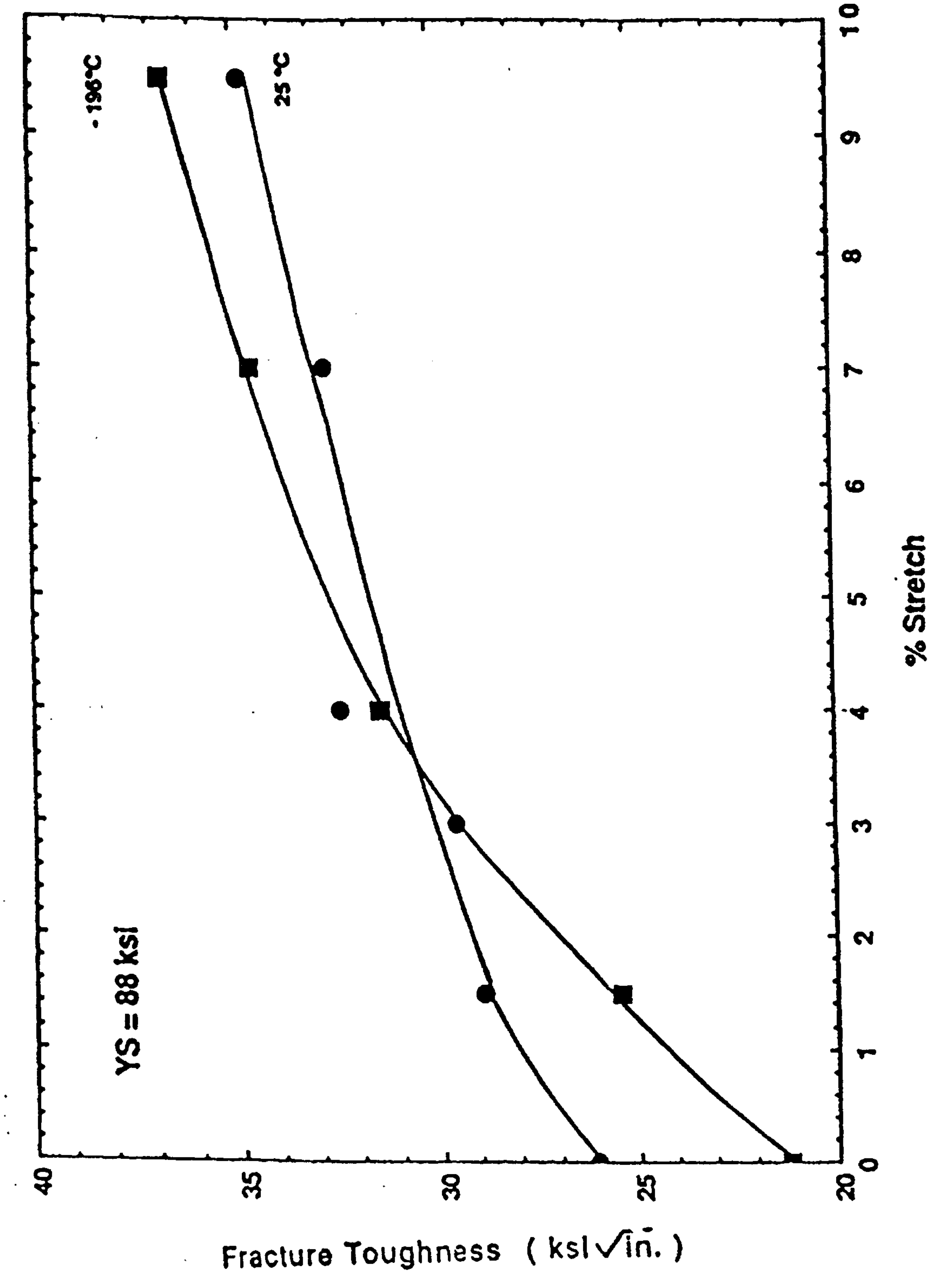
-196°C
25°C
YS = 88 ksi
0
1
2
3
4
5
6
7
8
9
10
% Stretch
40
35
30
25
20
Fracture Toughness (ksi√in.)

FIG. 5

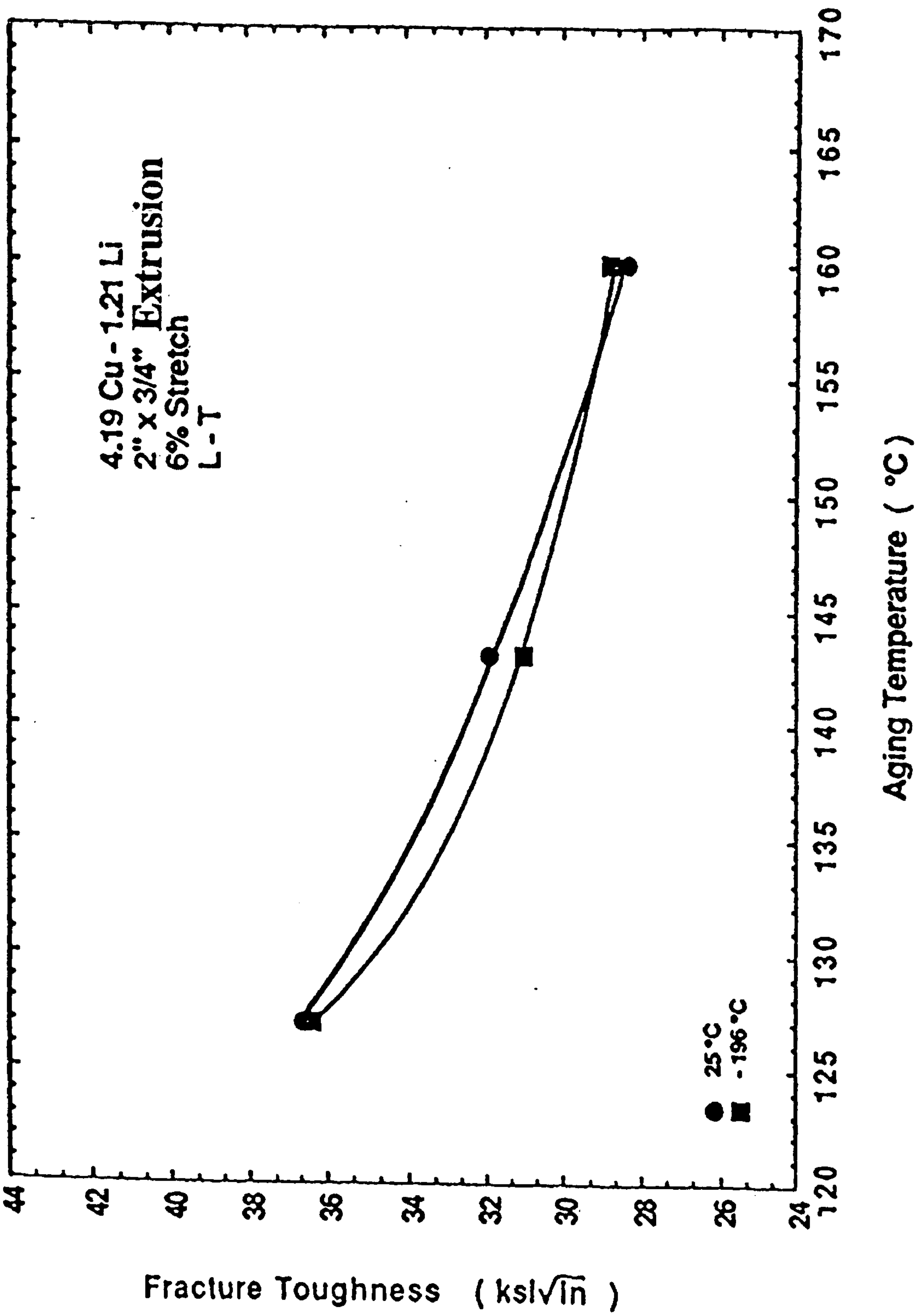
4.19 Cu - 1.21 Li
2" x 3/4" Extrusion
6% Stretch
L - T
● 25 °C
■ -196 °C
Aging Temperature (°C)
120
125
130
135
140
145
150
155
160
165
170
Fracture Toughness (ksi√in)
44
42
40
38
36
34
32
30
28
26
24

FIG. 6

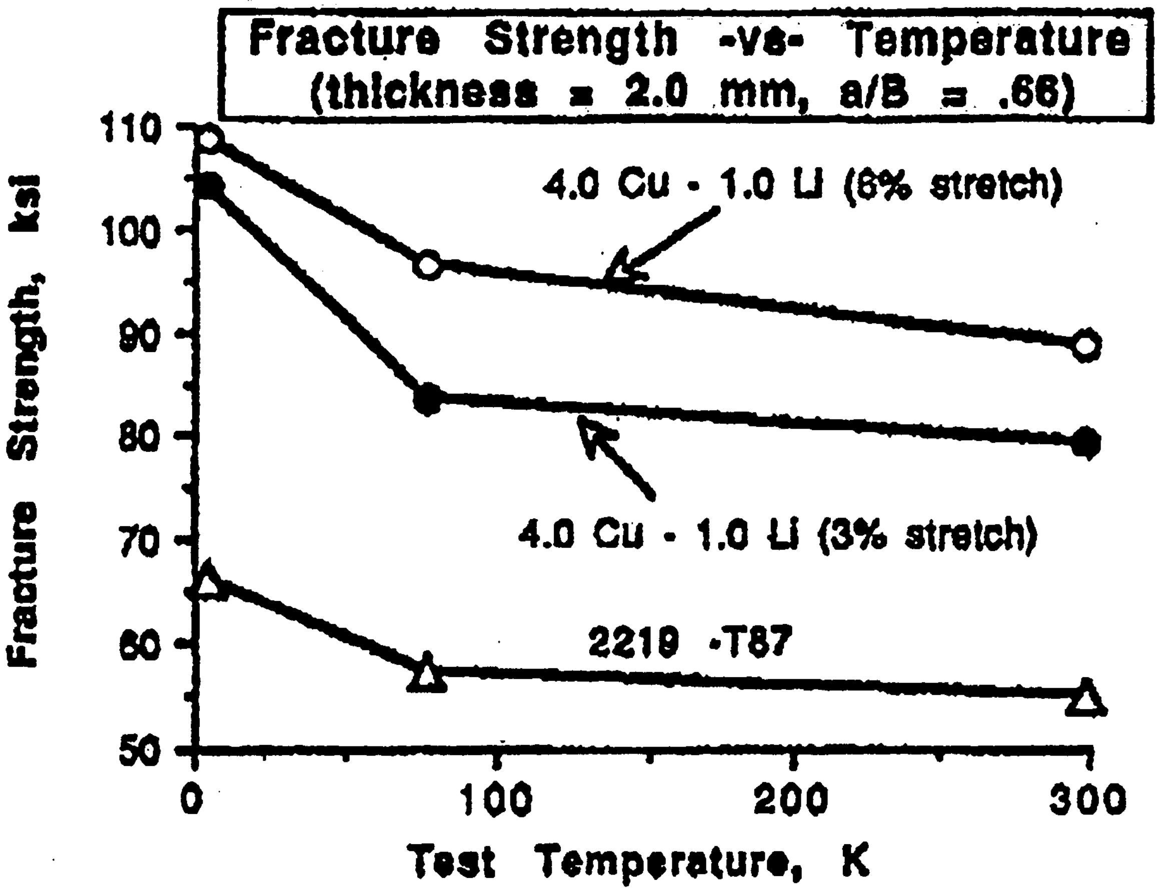
Fracture Strength -vs- Temperature
(thickness = 2.0 mm, a/B = .66)
Fracture Strength, ksi
110
100
90
80
70
60
50
0
100
200
300
Test Temperature, K
4.0 Cu - 1.0 Li (6% stretch)
4.0 Cu - 1.0 Li (3% stretch)
2219 -T87

FIG. 7

AL-CU-LI ALLOYS WITH IMPROVED CRYOGENIC FRACTURE TOUGHNESS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a Continuation-In-Part of U.S. patent application Ser. No. 08/032,158, now abandoned, filed Mar. 12, 1993, which is a continuation of U.S. application Ser. No. 07/493,255 filed Mar. 14, 1990, now abandoned, which is a Continuation-In-Part of U.S. patent application Ser. No. 07/327,666 filed Mar. 23, 1989, now U.S. Pat. No. 5,259,897 Continuation-In-Part of U.S. patent application Ser. No. 07/233,705 filed Aug. 18, 1988, now abandoned.

FIELD OF THE INVENTION

The present invention relates to aluminum-copper-lithium alloys having improved fracture toughness at cryogenic temperatures. More particularly, through control of composition and processing parameters, alloys are provided that exhibit improved fracture toughness and strength at low temperatures, making them suitable for use in cryogenic tanks for space launch vehicles and the like.

BACKGROUND OF THE INVENTION

Aluminum-copper-lithium alloys are under consideration as replacements for conventional aluminum alloys in launch systems. Currently, launch vehicles are constructed primarily from Aluminum Association registered alloys 2014 (Titan) and 2219 (Space Shuttle External Tank). Most of the dry weight of such launch systems, i.e., excluding propellant, is in propellant containment. For state of the art systems such as the Space Shuttle External Tank and the planned Titan IV cryogenic upper stage, the preferred propellant system is liquid hydrogen and liquid oxygen, which are each cryogenic liquids. It is therefore important for the structural alloy for such propellant containment to have both high strength and high toughness at cryogenic service temperatures. Furthermore, it is particularly advantageous for the alloy to have substantially equal or greater strength and toughness at cryogenic temperatures than at ambient temperature in both the parent alloy and any weldments. The ability to achieve higher fracture toughness and strength at cryogenic temperatures enables the structural proof test for the tank to be conducted more inexpensively at ambient rather than at cryogenic temperatures. If both strength and toughness are substantially the same or greater at cryogenic temperatures, a successful room temperature proof test ensures that neither strength-overload-induced nor toughness-limited-induced failure will occur at cryogenic service temperatures.

Cold work induced after solution heat treatment and quenching but before artificial aging is known to affect the mechanical properties of Al—Cu and Al—Cu—Li alloys. The most common way to induce such cold work is by plastically stretching axisymmetric product forms such as extrusions, sheet, and plate. The stretch, typically performed at room temperature, serves the dual function of straightening the product by plastic offset and providing dislocations that serve as nucleation sites for high-aspect-ratio strengthening precipitates, e.g., platelets, laths, etc., thereby increasing strength. Stretch is also known to increase room temperature toughness in Al—Cu and Al—Cu—Li alloys, but its effect on cryogenic toughness has not been reported to our knowledge.

Several aluminum-copper-lithium alloys have been commercialized. These include Aluminum Association (AA) registered alloys 2020, 2090, 2091, 2094, 2095, 2195, and 8090.

Alloy 2020 has a nominal composition, in weight percent, of Al—4.5Cu—1.1Li—0.5Mn—0.2Cd and was registered in the 1950's. Although the alloy possessed a relatively low density and developed high strength, it also possessed very low levels of fracture toughness and ductility. These problems along with processing difficulties led to the withdrawal of the alloy from the Aluminum Association register.

Alloy 2090 comprising Al—(2.4–3.0)Cu —1.9–2.6)Li—(0–0.25)Mg—0.12Zr was designed as a low density replacement for high strength alloys such as 2024 and 7075. Although this alloy develops relatively high strength, it also possesses poor short transverse fracture toughness and poor short transverse ductility associated with delamination problems and has not yet had wide range commercial success.

Alloy 2091 comprising Al—(1.8–2.5)Cu— (1.7–2.3)Li—(1.1–1.9)Mg—0.12Zr was designed as a high strength, high ductility alloy. However, at heat treated conditions that produce maximum strength, ductility is relatively low in the short transverse direction. Additionally, the strength achieved by alloy 2091 in non-cold-worked tempers is below the strength attained by the alloy in cold-worked tempers.

Alloy 8090 comprising Al—(1.0–1.6)Cu—(2.2–2.7)Li—(0.6–1.3)Mg—0.12Zr was designed for aircraft applications in which exfoliation corrosion resistance and damage tolerance were required. However, alloy 8090's limited strength capability and poor fracture toughness have prevented the alloy from becoming a widely accepted alloy for aerospace and aircraft applications.

Alloy 2094 comprises Al—(4.4–5.2)Cu—(0.8– 1.5)Li—(0.25–0.6)Mg—(0.25–0.6)Ag—0.25max. Zn—0.1max.Mn—(0.04–0.18)Zr, while alloy 2095 comprises Al—(3.9–4.6)Cu—(1.0–1.6)Li—(0.25–0.6)Mg—(0.25–0.6)Ag—0.25max.Zn—0.10max.Mn—(0.04–0.18)Zr. Alloy 2195 is similar to alloy 2095, but has slightly lower Cu and Li limits. These alloys possess exceptional properties such as ultra-high strength, high modulus, good weldability, etc.

U.S. Pat. Nos. 5,032,359 and 5,122,339 and U.S. patent application Ser. Nos. 07/327,666 filed Mar. 23, 1989, 07/493,255 filed Mar. 14, 1990 and 07/471,299 filed Jan. 26, 1990, each of which are hereby incorporated by reference, disclose aluminum alloys containing copper, lithium, magnesium and other alloying additions. These alloys have been found to possess very favorable properties such as high strength, high modulus, good weldability and good natural aging response.

In view of the technological importance of using improved alloys at cryogenic temperatures, it would be desirable to provide a low density, aluminum-base alloy that has higher strength and fracture toughness relative to conventional aluminum alloys and both increased strength and increased fracture toughness at cryogenic temperatures in comparison to room temperature. The present invention has been developed in view of the foregoing and provides aluminum-copper-lithium alloys within defined compositional ranges that exhibit improved combinations of cryogenic fracture toughness and strength when processed in accordance with the method of the present invention.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method of producing an aluminum-copper-lithium alloy that possesses improved fracture toughness and strength at cryogenic temperatures in comparison to room temperature.

Another object of the present invention is to provide a method of increasing the cryogenic fracture toughness and strength of an aluminum-base alloy, the method comprising the steps of providing a solution heat treated and quenched aluminum-base alloy within certain compositional ranges, working the alloy and artificially aging the alloy a sufficient amount to produce the desired increase in strength and fracture toughness at cryogenic temperatures.

Another object of the present invention is to provide an aluminum-copper-lithium alloy having improved fracture toughness and strength at cryogenic temperatures in comparison to room temperature.

Another object of the present invention is to provide a wrought aluminum-base alloy having increased cryogenic fracture toughness and strength, wherein the alloy is worked and artificially aged a sufficient amount to achieve the desired increase in fracture toughness and strength at cryogenic temperatures. In addition, the amounts of copper, lithium and other elements present in the alloy are controlled in order to achieve the desired improvement in properties at cryogenic temperatures.

Another object of the present invention is to provide a container for holding cryogenic materials such as liquid hydrogen, liquid oxygen, and liquid nitrogen, wherein the container is made of an aluminum-copper-lithium alloy that possesses improved fracture toughness and strength at cryogenic service temperatures.

In accordance with the present invention then, in one aspect there is provided a method for producing an improved aluminum-based alloy comprising the steps of:

a) providing a solution heat treated and quenched aluminum-base alloy consisting essentially of from 2.0 to 6.5 weight percent Cu, from 0.2 to 2.7 weight percent Li, and the balance aluminum and incidental impurities; and

b) at least one of working and artificially aging said alloy in an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature.

In accordance with another embodiment of the invention there is provided a wrought aluminum-base alloy consisting essentially of from 2.8 to 4.8 weight percent Cu, from 0.4 to 1.5 weight percent Li, from 0.2 to 1.0 weight percent Mg, and the balance aluminum and incidental impurities, wherein said alloy is worked, artificially aged, or worked and artificially aged an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature.

In accordance with still another embodiment of the present invention, there is provided a cryogenic material-holding container made from an alloy consisting essentially of from 2.8 to 4.5 weight percent Cu, from 0.4 to 1.5 weight percent Li, from 0.2 to 1.0 weight percent Mg, and the balance aluminum and incidental impurities, wherein said alloy is worked, artificially aged, or worked and artificially aged an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graph of fracture toughness versus yield strength for an alloy at room temperature and at cryogenic temperature. The graph demonstrates that fracture toughness of the alloy increases at cryogenic temperature when the alloy is artificially aged to a lower yield strength, but cryogenic fracture toughness decreases relative to that at room temperature when the alloy is artificially aged to a higher yield strength.

FIG. **2** is a graph of fracture toughness versus lithium content for alloys at room temperature and at cryogenic temperature. The graph shows an increase in cryogenic versus room temperature fracture toughness for alloys having a lower lithium content, but no discernable increase in cryogenic fracture toughness for alloys having a higher lithium content.

FIG. **3** is a graph of fracture toughness versus magnesium (Mg) content for alloys at room temperature and at cryogenic temperature. The graph shows an increase in cryogenic versus room temperature fracture toughness for all of the alloys.

FIG. **4** is a graph of fracture toughness versus temperature for an alloy that has been stretched various amounts. The graph demonstrates a decrease in cryogenic versus room temperature fracture toughness when the alloy is stretched a lesser amount, but an increase in cryogenic fracture toughness when the alloy is stretched a greater amount.

FIG. **5** is a graph of fracture toughness versus percentage of stretch for an alloy at room temperature and at cryogenic temperature. The graph shows a decrease in cryogenic versus room temperature fracture toughness at lower stretch levels, but an increase in cryogenic fracture toughness at higher stretch levels.

FIG. **6** is a graph of fracture toughness versus aging temperature for an alloy at room temperature and at cryogenic temperature. The graph shows that both room temperature and cryogenic fracture toughness increase as aging temperature decreases.

FIG. **7** is a graph of fracture strength versus temperature for an alloy of the present invention that has been stretched varying amounts. In addition, fracture strength versus temperature for a conventional alloy is shown. The graph demonstrates an increased improvement in cryogenic fracture strength when this alloy of the present invention is stretched a greater amount. Furthermore, a significant improvement in both strength and fracture toughness of the present alloy in comparison to the conventional alloy is shown.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the control of composition, fabrication and heat treating of aluminum-copper-lithium alloys in order to produce improved cryogenic fracture toughness and strength properties. In accordance with the present invention, a wrought aluminum-copper-lithium alloy is provided in which fracture toughness at cryogenic temperatures is higher than, or equal to, that at room temperature. In addition, strength at cryogenic temperatures is higher than that at room temperature. This combination of improved fracture toughness and strength at cryogenic temperatures is defined in accordance with the present invention as the "desirable cryogenic fracture toughness trend". The desirable trend can be attained by controlling the levels of copper and lithium in the alloys, and by controlling processing parameters such as stretch, aging and recrystallization of the alloys.

The term "cryogenic temperature" is defined in accordance with the present invention to include temperatures significantly below room temperature and typically below 0° C. Thus, the temperatures at which hydrogen (−253° C.), oxygen (−183° C.) and nitrogen (−196° C.) become liquid are included as cryogenic temperatures. For purposes of experimental evalution, a temperature of −196° C. is considered as a cryogenic temperature. Room temperature is defined in accordance with its common usage and includes temperatures of from about 20° to about 25° C. For purposes of experimental evaluation, a temperature of 25° C. is considered to be room temperature.

In addition to aluminum, copper and lithium, the alloys of the present invention may, in certain preferred embodiments, contain magnesium, silver, zinc, and combinations thereof, along with other alloying elements such as grain refiners, dispersoid forming elements and nucleation aids. Compositional ranges of the alloying additions of the present alloys are given below in Table 1. Unless stated otherwise, all composition values herein are in weight percent.

TABLE 1

	Compositional Ranges of Alloys (wt. %, balance Al)				
	Cu	Li	Ag	Mg	Zn
Broad	2.0–6.5	0.2–2.7	0–4.0	0–4.0	0–3.0
Preferred	2.8–4.8	0.4–1.5	0–0.8	0.2–1.0	0–1.0
Most Pref.	3.0–4.5	0.7–1.1	0–0.6	0.3–0.6	0–0.75

Other alloying additives such as Zr, Ti, Cr, Mn, Hf, Nb, B, Fe, Y, La, V, Mo, Se, Co, Ni, Cd, In, Sn, Ge and combinations thereof may be included in amounts up to a total of about 10 weight percent as long as such additions do not significantly impair the attainment of the desirable cryogenic fracture toughness trend. Grain refiners such as Zr, Ti, Cr, Mn, Hf, Nb, B, V and TiB_2 may be included in a preferred total amount of from about 0.01 to about 1.0 weight percent and more preferably from about 0.08 to about 0.3 weight percent. The amount of grain refining elements and/or dispersoid forming elements may be increased in excess of 1.0% when powder metallurgy processing is employed, e.g., rapid solidification, mechanical alloying, and reaction milling. Zirconium and titanium are particularly preferred as grain refining additions, with Zr also being beneficial as a recrystallization inhibitor.

In accordance with the present invention, alloys were prepared having compositions as set forth in Table 2. Although not listed in Table 2, aluminum makes up the balance of each composition.

TABLE 2

	Alloy Compositions (wt. %)						
Alloy	Cu	Li	Ag	Mg	Zn	Zr	Ti
A	6.18	1.35	0.41	0.40	0	0.16	0
B	4.52	1.29	0.40	0.36	0	0.14	0.03
C	4.13	1.27	0.40	0.40	0	0.14	0.02
D	4.38	1.04	0.38	0.38	0	0.14	0.03
E	5.70	1.29	0	0.34	0	0.15	0.04
F	4.01	0.84	0	0.40	0	0.14	0.03
G	6.00	1.00	0.38	0.36	0	0.14	0.04
H	4.23	0.73	0.40	0.34	0	0.15	0.02
I	4.28	0.85	0.36	0.40	0	0.14	0.03
J	3.95	1.03	0.39	0.37	0	0.14	0.03
K	4.19	1.21	0.37	0.38	0	0.14	0.04
L	4.00	1.41	0.38	0.37	0	0.14	0.03
M	3.78	1.81	0.40	0.34	0	0.15	0.03
N	4.04	0.86	0.38	0.24	0	0.14	0.03
O	4.28	0.84	0.36	0.38	0	0.14	0.03
P	4.31	0.80	0.36	0.38	0	0.14	0.03
Q	4.04	0.85	0.38	0.60	0	0.15	0.03
R	4.90	1.15	0.40	0.40	0	0.14	0.02
S	3.58	0.93	0.35	0.34	0.22	0.15	0.04
T	3.79	0.92	0.34	0.34	0.40	0.15	0.03
U	4.00	1.00	0.40	0.40	0	0.14	0.02
V	3.62	0.99	0.35	0.36	0	0.15	0.04
W	3.61	0.91	0	0.33	0.39	0.15	0.04
X	2.8	0.86	0	0.38	0.65	0.14	0.02
Y	3.5	0.79	0	0.41	0.75	0.14	0.02
Z	2.16	0.80	0	0.38	0	0.14	0.03
AA	3.18	0.78	0	0.36	0	0.15	0.02
BB	3.56	0.29	0	0.39	0	0.14	0.03
CC	3.43	0.56	0	0.35	0	0.14	0.03
DD	3.41	1.12	0.38	0.36	0	0.14	0.03
EE	4.47	0.95	0.43	0.43	0	0.14	0.02
FF	4.99	1.23	0.38	0.46	0	0.17	0.04
GG	5.20	1.00	0.40	0	0	0.16	0

Unless otherwise indicated, each of the above listed compositions was prepared as follows. The alloys were cast as 23 kilogram (50 lb.), 16.5-cm (6.5-inch) diameter ingots using an inert gas induction melting furnace. The ingots were homogenized at 450° C. for 16 hours plus 504° C. for 8 hours, scalped and extruded into 1.9×5.1 cm (¾×2 inch) rectangular bars at a preheat temperature of 370° C. (700° F). The extrusions were solution heat treated for one hour at a temperature just below the solidus and then water quenched. Varying amounts of stretch of from 0–9.5% were applied to the alloys and varying artificial aging temperatures and times were employed.

The term "worked" as used in accordance with the present invention is defined as the introduction of the equivalent of up to about 12 percent stretch to an alloy. In addition to stretching, other means of working can be used such as rolling, roll forming, bump forming, spinning, shot peening and the like. Preferred amounts of stretch, or the equivalent thereof, range from about 3 to about 9 percent, with from about 4.5 to about 7 percent generally being more preferred, depending on the alloy composition, the geometry of the part, and other processing parameters. Working of the alloys is typically carried out at room temperature (cold work), but both cryogenic and warm temperatures may be suitable.

Artificial aging temperatures may vary, with temperatures of less than about 120° C. to greater than about 180° C. being satisfactory for most alloys. Artificial aging temperatures of from about 125° to about 145° or 150° C. are preferred in order to promote the desirable cryogenic fracture toughness trend. Aging times are dependent on aging temperature and may extend up to a point at which the length of time becomes impractical. Aging times of from about 0.25 to about 500 hours may typically be used, with from about 2 to about 48 hours being preferred, and about 4 to about 24 hours being most preferred, depending on the alloy composition and other processing parameters.

The alloys of the present invention are typically cast into ingot form or billet form. The term "ingot" as used herein is broadly defined as a solid mass of alloy material. The term "billet" as used herein includes hot worked, semi-finished products suitable for subsequent working by such methods as rolling, extruding, forging, etc. While the formation of ingots or billets of the present alloys by casting techniques is preferred, the alloys may also be provided in ingot or billet form consolidated from fine powders or particulates. The powder or particulate material can be produced by such processes as atomization, mechanical alloying, melt spinning, splat cooling, plasma deposition and the like.

The alloys of the present invention may be provided in various known wrought forms, including extrusions, sheet, plate, forgings and the like. The term "wrought" alloy as used herein is defined as a product that has been subjected to mechanical working by such processes as extruding, rolling, forging, spin-forming and the like. The term "sheet" is defined in accordance with the present invention as a rolled product having a generally rectangular cross section with a thickness of from about 0.006 to about 0.249 inch, and having sheared, slit or sawed edges. The term "plate" is defined in a similar manner as sheet, with the exception that the thickness is about 0.250 inches or greater.

The following examples illustrate various aspects of the present invention and are not intended to limit the scope of the invention. Unless stated otherwise, all yield strength values are in the longitudinal direction and all toughness values are in the L-T orientation. The term "L-T" means that the loading direction is parallel to the working direction and that the direction of crack propagation is along the longest axis of the product that is perpendicular to the working direction. Most fracture toughness values are plane strain fracture toughness measured from precracked compact tension specimens. Some fractured specimens failed the ASTM B399 plasticity check so the toughness is described as K_Q rather than K_{Ic} (ASTM B399). However, the flat nature of the fractures suggests that the K_Q values are close to K_{Ic} values.

Most cryogenic tanks used for launch systems use aluminum alloys of sufficiently thin gages that service loading conditions are under plane stress. Plane stress fracture toughness is thickness dependent and it is difficult to obtain such toughness values with sufficiently low scatter to discern subtle differences in toughness caused by alloying and processing effects. To circumvent such difficulties, plane strain fracture toughness (K_{Ic}) was measured from thicker gages to assess toughness and the cryogenic toughness trend because K_{Ic} is a fundamental materials parameter and is largely unaffected by differences in specimen size. In addition, K_{Ic} values generally display lower scatter than do other measures of toughness.

EXAMPLE 1

An extrusion of Alloy A (6.18 wt % Cu) was solution heat treated at 504° C. for 1 hour, quenched in water (WQ) at 20° C. incubated for 1 hour at 20° C., stretched longitudinally 3% and artificially aged at 160° C. for 6 hours. A longitudinal yield strength (YS) of 94.3 ksi and an ultimate tensile strength (UTS) of 98.5 ksi is achieved, with an elongation of 5% at 20° C. i.e., underaged T8 properties. The 20° C. plane strain fracture toughness (K_{Ic}), measured on fatigue precracked compact tension specimens in the L-T orientation is 18.6 ksi$\sqrt{in}$. At −196° C. the YS and UTS increase to 116 ksi and 123 ksi, respectively. The strength of a given aluminum alloy is expected to increase with decreasing test temperature provided that the alloy does not experience premature brittle fracture, which is a manifestation of low toughness or ductility. Ductility at −196° C. decreases to 2.2% elongation and toughness decreases to 17 ksi$\sqrt{in}$. This exemplifies the undesirable cryogenic fracture toughness trend.

EXAMPLE 2

Alloy A was aged to a higher strength level than in Example 1, i.e., aged at 160° C. for 24 hours, giving a 20° C. YS of 98.7 ksi, UTS of 101.5 ksi and elongation of 5.4%. Fracture toughness at 20° C. at this higher strength level is quite low at 13.4 ksi$\sqrt{in}$. This toughness is sufficiently low such that the alloy would not be competitive for toughness-critical applications at this strength level. Consequently, toughness at −196° C. was not measured, but the cryotoughness trend would be expected to be undesirable.

EXAMPLE 3

Alloy B was processed similarly to Alloy A in the preceeding examples. Alloy B has a similar composition to that of Alloy A, except that Cu content is significantly lower at 4.52 wt %. Alloy B's 20° C. underaged T8 properties after a slightly underaged heat treatment (16 h at 160° C.) are higher in strength, at 99.7 YS and 102 UTS, and higher in tensile elongation at 6.4%. Alloy B's 20° C. fracture toughness is also higher at a K_{Ic} of 22.3 ksi$\sqrt{in}$ at this higher strength level. This is significant because the alloy was aged 5 ksi stronger than Alloy A in Example 1, where the toughness at 20° C. was only 18.6 ksi$\sqrt{in}$. These improvements in room temperature ductility and toughness are believed to result from the decrease in Cu content. At −196° C., YS increases to 122 ksi, UTS increases to 130 ksi and ductility increases to 7.4% elongation. On the other hand, at −196° C. toughness decreases very slightly to 21.4 ksi$\sqrt{in}$, virtually a flat trend at an extremely high strength level. Thus, decreasing the Cu content from 6.18 to 4.52% comes very close to producing the desirable cryogenic fracture toughness trend with material stretched 3% and aged to a 20° C. YS of about 100 ksi.

EXAMPLE 4

Alloy B was aged for 16 hours at 160° C. as in Example 3, but was stretched 5% instead of 3%. By stretching 5%, aging kinetics are increased such that artificial aging for 16 h at 160° C. now gives peak strength (103 ksi Ys, 105 ksi UTS with 6% el). Fracture toughness at 20° C. is 20.2 ksi$\sqrt{in}$ at this ultra-high strength level. However, toughness increases significantly at −196° C. to 25.0 ksi$\sqrt{in}$. Thus, the desirable trend is achieved at an extremely high strength level by lowering the Cu to 4.52% and increasing the stretch level to 5%.

EXAMPLE 5

Alloy C is similar to Alloys A and B but has a Cu content of 4.13%. When similarly processed (SHT 511° C. for 1 h, WQ, stretched 3% and aged for 12 h at 160° C.), it is slightly weaker in the T8 temper at 94 ksi YS and 98 ksi UTS, but has better 20° C. fracture toughness than that of the 4.52% Cu Alloy B, i.e., 24.5 instead of 22.3 ksi$\sqrt{in}$. At −196° C., YS increases to 115 ksi, but fracture toughness decreases to 19.3 ksi$\sqrt{in}$ (see FIG. 1). Thus, although the decrease in Cu to 4.13% increases toughness at 20° C. at the 3% stretch level, the desirable cryogenic fracture toughness trend is not achieved at the 94 ksi YS level.

EXAMPLE 6

Alloy C is underaged to a 20° C. YS of 89 ksi, at which point the onset of the desirable trend is achieved (fracture toughness of 33.9 ksi√in at 20° C. and 34.3 ksi√in at −196° C.). Underaging Alloy C further to 86 ksi YS at 20° C. increases toughness and clearly results in the desirable trend. That is, 20° C. toughness is 38.7 ksi√in, while −196° C. toughness is 40.4 ksi√in (see FIG. 1). This represents an excellent example of the desirable cryogenic fracture toughness trend at both a high strength and a high toughness level.

The effect of lower Cu on the desirable cryogenic fracture toughness trend is shown in the preceeding examples. However, it is noted that the desirable trend can be attained at higher Cu levels with greater stretch, as shown in the following examples.

EXAMPLE 7

Alloy D is similar in composition to alloy B except that the Li content is slightly lower. Part of this extrusion was stretched 3% and part 6%. The desirable trend is just about attained at a 20° C. YS of 88 ksi at the 3% stretch level, but it is reached very easily at the 93 ksi 20° C. YS level with 6% stretch (see Table 3). Furthermore, the desirable trend is almost achieved at 98.5 ksi YS. The desirable trend is more readily achieved because of the higher stretch level and, in addition, the lower Li content which will be further illustrated later.

The greater ease at which the desirable trend can be achieved with decreasing Cu content is also observed in the Al—Cu—Li—Mg system. This can be seen in Examples 8 and 9 below.

EXAMPLE 8

Alloy E is similar in composition to Alloy A except that Alloy E is Ag—free. Alloy E's peak 20° C. strength with 3% stretch can be attained by aging for 16 h at 160° C. (95.2 ksi YS, 98.3 ksi UTS and 6% el). The peak strength of Alloy E is slightly lower than that of Alloy A because of the absence of Ag in Alloy E. At −196° C., strength increases to 114 ksi YS and 123 ksi UTS, with a decrease in elongation to 4.0%. Toughness at 20° C. is 16.9 ksi√in, decreasing slightly to 16.6 ksi√in at −196° C. This toughness can be increased with only a slight strength penalty by underaging, e.g., aging for 6 h at 160° C. producing a YS of 94.2 ksi, UTS of 98.6 ksi, elongation of 7.9% and K_Q of 25.4 ksi√in at 20° C. The properties at −196° C. are 111 ksi YS, 123 ksi UTS, 7.5% el and K_Q of 23.0 ksi√in. The desirable trend is not quite achieved in either case.

EXAMPLE 9

Alloy F is similar in composition to Alloy E, but is significantly lower in Cu and Li content (see Table 2). The decrease in solute produces a lower peak YS at 20° C. of 90 ksi compared to that of Alloy E. In a slightly underaged condition after 6% stretch (aged at 143° C. for 30 h), 20° C. properties are 88.1 ksi YS, 90.8 ksi UTS, 10.5% el and 39.4 ksi√in toughness. At −196° C., YS increases to 104.8 ksi, UTS increases to 111.2 ksi and elongation increases to 11.2%. Importantly, toughness increases to 47.1 ksi√in, an excellent example of the desirable trend. With slightly less aging of Alloy F to a 20° C. YS of 85 ksi, a 20° C. K_{Ic} of 39.7 ksi√in is achieved, while a −196° C. toughness of 51.0 ksi√in is achieved. Thus, the desirable trend is achieved and the teaching in Examples 1–7 for Al—Cu—Li—Ag—Mg alloys applies to Al—Cu—Li—Mg alloys.

EXAMPLE 10

Alloy G is similar in composition to Alloy A (high Cu content) but has a lower Li content of 1.0% (see Table 2). When processed similarly to Alloy A (370° C. preheat temperature for extrusion, 504° C. SHT, WQ, stretch 3% and age for 16 h at 160° C.), similar tensile properties to those of Alloy A are obtained, but with higher toughness. That is, at 25° C. a YS of 103 ksi, UTS of 105 ksi, elongation of 3.8% and K_{Ic} of 18.7 ksi√in are obtained. This toughness is higher than the 13.4 ksi√in attained for Alloy A at the ultra-high strength level (see Example 2). At −196° C., similar properties to those of Alloy A are once again obtained (123 ksi YS, 128 ksi UTS and 3.6% el), but with a slightly higher toughness of 19.2 ksi√in than Alloy G at 25° C. Thus, even with such a high Cu content, a flat or desirable cryogenic fracture toughness trend can be attained by lowering the Li content. The benefits of underaging can also be seen by aging alloy G for 6 h at 160° C. instead of 16 h. Strength at 25° C. is still high at a YS of 87.6 ksi and a UTS of 92.8 ksi, but elongation increases to 8% and toughness increases to 30.0 ksi√in. At −196° C., strength is higher (113 ksi YS, 121 ksi UTS and 6.5% el), but toughness, increases to 32.6 ksi√in, clearly the desirable trend. Thus, underaging trades strength for toughness, but, unexpectedly, the desirable cryogenic toughness trend is more readily achieved. Importantly, the desirable trend can be achieved at relatively high Cu levels.

EXAMPLE 11

This example examines the effect of Li content on the desirable cryogenic toughness trend. In particular, lowering the Li content increases the ease with which the desirable trend is achieved. This can be seen in FIG. 2, in which the compositions of several alloys are very similar except for Li content. The alloys nominally contain Al—4.0Cu—XLi—0.4Ag—0.4 Mg—0.14Zr (see Alloys H–M in Table 2). Each alloy was preheated to 370° C., extruded at a ram speed of 0.25 cm/s (0.1 in/s) in a 16.2-cm (6.375-inch) diameter container to 5.1×1.9 cm bar (2×¾ inch). Each bar was solutionized at 4°–7° C. below its specific solidus temperature, water quenched at 25° C. and stretched 6%. Aging studies at 143° C. were performed for each extrusion and then each was aged at 143° C. to a target room temperature YS of 90 ksi. Actual YS values obtained were similar, with a low of 88.5 ksi and a high of 92.8 ksi. As shown in FIG. 2, toughness at 25° C. and −196° C. each decrease monotonically with increasing Li content. For Li contents of greater than about 1.2%, the toughness trend is approximately flat in each case. However, at Li levels less than about 1.2%, toughness at −196° C. is consistently greater than that at 25° C., i.e., the desirable trend is clearly achieved.

EXAMPLE 12

This example examines the effect of Mg content on the desirable cryogenic toughness trend. Castings of nominal composition Al—4Cu—0.8Li—0.4Ag—XMg—0.14Zr (see Alloys N–Q in Table 2) were prepared under similar conditions. The alloys were preheated at 370° C. and extruded in a 16.2-cm (6.375-inch) diameter container at a ram speed of 0.25 cm/s (0.1 in/s) into 5.1×1.9 cm (2×¾ inch) bar. The heats were solutionized at 3°–6° C. below the individual solidus temperature, i.e., solutionized at 511°–515° C. water quenched at 25° C. and stretched 6%. They were then aged at 143° C. to various YS levels. The properties at the nominal 90 ksi YS level, shown in FIG. 3, indicate that fracture toughness at 20° C. increases with Mg content. Toughness at −196° C. also generally increases with Mg content. The alloys were then tested for fracture toughness at various strength levels at 25 and −196° C. At 25° C. strength-toughness combinations clearly improve with increasing Mg content. At −196° C., strength-toughness combinations improve by raising the Mg content from 0.2 to 0.4 wt %. At 0.6 wt % Mg, the data vary more, but also show higher toughness and the desirable trend. The desirable trend is achieved for each Mg level from 0.2 to 0.6%, but the 0.4 and 0.6% Mg-containing alloys can be aged to higher strengths, i.e., 97–98.1 ksi YS compared to 91 ksi YS for the 0.2% Mg-containing alloy. As can be seen, the toughness values at −196° C. are extremely high for all of these alloys. In addition, underaging also facilitates the ability to attain the desirable cryogenic fracture toughness trend with these alloys of varying Mg content.

EXAMPLE 13

This example examines the effect of cold stretch on the desirable cryogenic fracture toughness trend. Alloy R, having a composition of Al—4.9Cu—1.15Li—0.4Ag—0.4Mg—0.14Zr, was cast and extruded at a preheat temperature of 370° C. (700° F.) in a 16.2-cm (6.375-inch) diameter container at a nominal ram speed of 0.25 cm/s (0.1 in/s) into 5.1×1.9 cm (2×0.75 inch) rectangular bar. The extrusion was solution heat treated at 504° C. for ¾ h, water quenched at 25° C., and a portion of the bar was removed (with 0% stretch). The remaining bar was then stretched 1.5%, a piece was cut off, stretched again with material cut off, and this procedure was repeated giving sections with stretch levels of 0, 1.5, 4, 7 and 9.5%. The artificial aging response was determined for each stretch level and portions of each extrusion were heat treated to a 20° C. YS of 88 ksi. Plane strain fracture toughness from fatigue precracked CT specimens was measured at each stretch level at 20° C. and −196° C. Toughness at 20° C. was found to increase with increasing stretch (see FIG. 4). The undesirable trend was attained at 0, 1.5, and 4% stretch (see FIGS. 4 and 5) at this strength level. However, at the higher stretch levels of 7 and 9.5%, the desirable cryogenic fracture toughness trend is attained. Fractographic and transmission microscopy were performed on each sample. While not intending to be bound by any particular theory, it is believed that stretch refines strengthening precipitation in the grain interiors while decreasing precipitation of coarser precipitates on grain and subgrain boundaries. Such coarse precipitates are known to lower room temperature toughness. However, the surprising result of increased cryogenic toughness, in comparison to room temperature toughness, with increased stretch level is not understood. For Alloy R at the 88 ksi YS stretch level, the cryogenic toughness trend switches from undesirable to desirable at around 4% stretch (see FIG. 5). This switchover point could be moved to lower stretch levels by underaging to lower YS levels, decreasing Cu and/or Li content or, to a lesser extent, decreasing aging temperature.

EXAMPLE 14

The current teachings for attaining the desirable cryogenic toughness trend as shown in Examples 1–13 for Al—Cu—Li—Ag—Mg—Zr and Al—Cu—Li—Mg—Zr alloys also apply to similar alloys containing Zn. Alloy S, which is similar to high toughness Al—Cu—Li—Ag—Mg—Zr Alloy J in that it has relatively low Cu and Li and has been stretched 6%, has about a quarter percent Zn. Zinc has been found to produce beneficial effects on the alloy such as increasing aging response. When the alloy is artificially aged at 143° C. for 20 h, it attains a 25° C. YS of 91.2 ksi, a UTS of 94.2 ksi and an elongation of 12.4%. Just as is the case for Zn-free alloys, strength increases at cryogenic temperatures (YS=112.1 ksi, UTS=118.9 ksi and el=5.2% at −196° C.). Importantly, the high 25° C. toughness of 38.9 ksi√in increases to 43.6 ksi√in at −196° C., an excellent example of the desirable cryogenic toughness trend. Toughness could be increased further by lowering the Cu and/or Li content.

EXAMPLE 15

Alloy T is similar in composition to Alloy S, except that the Zn content is roughly doubled to 0.40%. The alloy was aged for 28 hours at 143° C., which is slightly further along the aging curve than the previous example of Alloy S. Otherwise, the alloy was processed the same. A slightly higher 25° C. YS of 94.0 ksi, UTS of 95.8 ksi and elongation of 9.9% are achieved. At −196° C., YS increases to 114 ksi and UTS increases to 119.8 ksi, with 9.4% elongation. Importantly, the high 25° C. toughness of 35.9 ksi√in is virtually unchanged at 36.1 ksi√in at −196° C., indicating that the threshold of the desirable trend has been reached. The fact that this Zn-containing Al—Cu—Li—Ag—Mg alloy has been aged slightly longer than the previous example of Alloy S, and therefore goes from a very desirable trend to a flat trend, is the same behavior observed in the Al—Cu—Li—Ag—Mg and Al—Cu—Li—Mg alloys. Nevertheless, a desirable or flat trend is attained for each Zn-containing alloy at very high strength levels.

EXAMPLE 16

This example examines the effect of aging temperature on the desirable cryogenic fracture toughness trend. Alloy K having a composition of Al— 4.19Cu—1.21Li—0.37Ag—0.38Mg—0.14Zr—0.04Ti was cast, extruded, solutionized, quenched and stretched 6% as described in Example 11. Samples were then artificially aged at varying temperatures of from 127° to 160° C. to attain a room temperature YS of about 90 ksi. One sample was aged at 127° C. for 100 hours to achieve a room temperature YS of 88.4 ksi, a UTS of 94.7 ksi, an elongation of 8.8% and a K_Q of 36.6 ksi√in. At −196°C., the sample aged at 127° C. attained a YS of 103.4 ksi, a UTS of 113.4 ksi, an elongation of 10.9% and a K_Q of 36.4 ksi√in. Another sample was aged at 143° C. for 22 hours to attain a 25° C. YS of 90.7 ksi, a UTS of 94.9 ksi, an elongation of 10.1% and a K_Q of 31.9 ksi√in. At −196° C., this sample attained a YS of 108.7 ksi, a UTS of 116.0 ksi, an elongation of 9.4% and a K_Q of 31.0 ksi√in. A third sample was aged at 160° C. for 4.5 hours to attain a 25° C. YS of 91.0 ksi, a UTS of 94 4 ksi, an elongation of 7.7% and a K_Q of 28 4 ksi√in. At −196° C., this sample achieved a YS of 108.6 ksi, a UTS of 115.5 ksi, an elongation of 8.7% and a K_Q of 28.8%. As shown in FIG. 6, for each of the above aging temperatures, the cryogenic fracture toughness trend is essentially flat for each aging temperature at this strength level. However, fracture toughness values at both room temperature and cryogenic temperature increase significantly as the aging temperature for the alloy decreases.

EXAMPLE 17

Alloy U having a composition of Al—4.0Cu—1.0Li—0.4Ag—0.4Mg—0.14Zr (virtually the same as Alloy J) was cast and rolled to 9.5 mm (0.375 in.) plate, solution heated at 510° C. (950° F.), quenched in water at 20° C. and either stretched 3% or 6%. Plate at each stretch level was aged at 143° C. to a 20° C. YS of 85 ksi. The plates were machined down to 2.0 mm to simulate anticipated flight gages for the External Tank of the Space Shuttle. To evaluate fracture toughness of the alloy at this thickness, the surface crack tension test (ASTM E740) was used. In this test, a central notch is electro-discharge machined and fatigue precracked to a predetermined semielliptical size by fatigue loading. The flaw was controlled so the crack-depth to plate-thickness ratio is 0.66, i.e., the flaw extends about two thirds through the thickness. The panel is then tested to failure in tension and the fracture stress is taken as a measure of toughness in this mostly plane stress specimen. Tests were performed in the T-L orientation to compliment earlier data in the L-T orientation. Panels of conventional alloy 2219-T87 were also tested for comparison. As shown in FIG. 7, both stretch levels display a significant toughness advantage over 2219-T87, the alloy currently used on the Space Shuttle External Tank. For example, the variant with 6% stretch has a 69% advantage over 2219 at a test temperature of 4K, which could translate directly to a structural weight savings in the tank membranes of that gage. It is noted that both stretch levels show the desirable trend for the 2.0 mm gage and that toughness increases with stretch level as was shown in the previous examples for extrusions.

EXAMPLE 18

Alloy V, comprising Al—3.62Cu—0.99Li—0.35Ag—0.36Mg—0.15Zr—0.04Ti, falls within the most preferred compositional range of the present invention. With 6% stretch and artificial aging at 143° C. for 26 hours, the alloy attains room temperature properties of 90.0 ksi YS, 91.5 ksi UTS, 8.7% elongation and 38.7 ksi√in K_{Ic}. At −196° C., the alloy attains properties of 114.8 ksi YS, 120.0 ksi UTS, 9.6% elongation and 40.7 ksi√in K_{Ic} (see Table 3), i.e., the desirable cryogenic fracture toughness trend is obtained.

EXAMPLE 19

Alloy W, comprising Al—3.61Cu—0.91Li—0.33Mg—0.39Zn—0.15Zr—0.04Ti, was stretched 6% and artificially aged at 143° C. for varying lengths of time as shown in Table 3. This alloy attains a peak strength of about 90 ksi, which is attained by aging for 26 hours at 143° C. At this aging temperature, strength does not change significantly for longer aging times. For example, increasing the aging time by about 70% to 44 hours only over-ages the alloy very slightly as 25° C. YS decreases to about 89 ksi (See Table 3). However, this increased aging has an adverse effect on the cryogenic fracture toughness trend. As can be seen in Table 3, the desirable cryogenic fracture toughness trend is essentially attained at the shorter aging time but is not attained at the longer aging time.

EXAMPLE 20

Alloys X and Y are Ag-free and contain Zn (see Table 2). As shown in Table 3, the room temperature strengths of these alloys are quite high, especially considering the relatively low alloying content of these alloys. Furthermore, the room temperature plane strain fracture toughnesses are well above 50 ksi√in. The toughnesses of these alloys are so high that valid L-T K_{Ic} toughness values are not obtained with the 2×¾ inch extruded bar samples. Each of Alloys X and Y are capable of attaining the desirable cryogenic fracture toughness trend.

EXAMPLE 21

Alloy Z contains 2.16% Cu (see Table 2). Significantly lower strengths are obtained with this low-copper variant as shown in Table 3. Although the desirable trend can be attained with this alloy, the strengths are less desirable than those for the alloys in aforementioned examples.

EXAMPLE 22

Alloy AA falls within the most preferred compositional range of the present invention (see Table 2). As shown in Table 3, high strengths are obtained at room temperature, especially considering the relatively low alloying content of the alloy. The room temperature plane strain fracture toughness is above 50 ksi√in. However, since the toughness is so high, valid L-T K_{Ic} toughness values are not obtained with the 2× ¾ inch extruded bar samples. Alloy AA is readily capable of attaining the desirable cryogenic fracture toughness trend.

EXAMPLE 23

Alloy BB and CC contain 0.29% Li and 0.56% Li, respectively. Otherwise, the alloys are very similar in composition (see Table 2). Alloy BB, containing the lower amount of Li, possesses significantly decreased room temperature strengths compared to Alloy CC, as shown in Table 3. Although each alloy could attain the desirable cryogenic fracture toughness trend, the lower Li content of alloy BB causes the alloy to have much lower strengths than alloy CC, and alloys in aforementioned examples.

From the foregoing examples it can be seen that the desirable cryogenic fracture toughness trend can be achieved in accordance with the present invention by controlling composition, stretch and artificial aging of the alloys. The effects of these parameters are set forth in Table 3.

EXAMPLE 24

Alloy DD is similar in composition to alloy S, except that it is Zn free and has a lower Cu content of 3.41% and a higher Li content of 1 12%. It was processed similarly to the other alloys in the study, but part of the extrusion was stretched 3% and the remainder 6%. The 3% stretch material was aged for 24 hours at 143° C., giving a 25° C. YS of 88.5 ksi and a K_Q of 29.8 ksi√in. (See Table III) At −196° C. YS increased to 108.4 ksi and K_Q increased to 41.6 ksi. The 6% stretch material was aged for 16 hours at 143° C. and achieved virtually the same 88.4 ksi YS and a K_Q value of 28.7 ksi√in at 25° C. At −196° C., YS increased to 107.2 ksi and toughness increased to 42.1 ksi√in for both the 3% and the 6% stretch materials. Thus, the desirable cryogenic fracture toughness trend was achieved in both cases. This example shows that with properly selected composition, similar results can be achieved at different stretch levels. Furthermore, with alloys of the present invention the desirable trend can be achieved at different stretch levels when heat treatment is carefully controlled. Note also that with an alloy of composition according to this teaching, the desirable trend can be attained at higher strength levels (e.g., 95.5 ksi 25° C. YS, see Table III)

EXAMPLE 25

Alloy EE is similar in composition to alloy D, and has the composition Al—4.47Cu—0.95Li—0.43Ag—0.43 Mg—0.14 Zr—0.02 Ti. It was processed similarly the alloys in the previous examples and, importantly, it was extruded to 2×0.75 in rectangular bar. The aspect ratio from this extrusion is a rather low 2.67 (i.e., 2÷0.75), so the long transverse properties would be expected to be fairly close to the short transverse properties.

A section of the bar was stretched 3% and aged at 160° C. for 6 hours, providing a 25° C. longitudinal YS of 86.5 ksi and L-T K_{Ic} of 40.7 ksi√in. These increased at −196° C. to

106.2 ksi YS and 49.3 ksi K_{Ic}, respectively. In the long transverse orientation, 25° C. YS was 70.5 ksi and T-L (i.e., long transverse toughness) K_{Ic} was 30.8 ksi$\sqrt{\text{in}}$. At −196° C., long transverse K_{Ic} increased to 36.4 ksi$\sqrt{\text{in}}$. Thus, the desirable cryogenic fracture toughness trend is achieved in both longitudinal and transverse orientation.

EXAMPLE 26

An alloy of composition FF (Al—4.99 Cu—1.23 Li—0.38 Ag—0.46 Mg—0.17 Zr—0.04 Ti) was welded by gas tungsten arc welding using filler wire of composition GG (Al—5.20 Cu—1.00 Li—0.40 Ag—0.16 Zr). Plane strain fracture toughness was measured from compact tension specimens orientated with crack propagation parallel and through the fusion zone, or parallel and through the heat affected zone (HAZ). These specimens are orientated in a T-L orientation. In addition, long transverse tensile testing was performed on specimens including both the fusion zone and the HAZ. Tests were performed at 25° C. and −196° C.

Weldment strength increased from 32.7 ksi YS, 51.4 ksi UTS with 6.9% elongation at 25° C. to 42.0 ksi YS, 63.6 ksi UTS, and 6.1% elongation at −196° C. In addition, fusion zone toughness was 19.0 ksi$\sqrt{\text{in}}$ at 25° C. increasing to 22.9 ksi$\sqrt{\text{in}}$ at 196° C. Moreover, HAZ toughness increased from 18.8 ksi$\sqrt{\text{in}}$ at 25° C. to 23.6 ksi$\sqrt{\text{in}}$ at −196° C. Thus, the desirable cryogenic toughness trend was attained on weldments.

TABLE 3

Properties For Varying Compositions With Varying Stretch And Artificial Aging

					Room temperature				−196° C.			
Alloy (wt. %)	Cu (wt. %)	Li (wt. %)	Stretch	Aging (°C. (h))	YS (ksi)	UTS (ksi)	El. (%)	K_{IC} (ksi$\sqrt{\text{in}}$)	YS (ksi)	UTS (ksi)	El. (%)	K_{IC} (ksi$\sqrt{\text{in}}$)
A	6.18	1.35	3	160 (6)	94.3	98.5	5.0	18.6	116.0	123.0	2.2	17.0
A	6.18	1.35	3	160 (24)	98.7	101.5	5.4	13.4				
B	4.52	1.29	3	160 (16)	99.7	102.0	6.4	22.3	122.0	130.0	7.4	21.4
B	4.52	1.29	5	160 (16)	103.0	105.0	6.0	20.2				25.0
C	4.13	1.27	3	160 (12)	94.0	98.0	8.5	24.5	113.0	120.5	8.1	19.3
C	4.13	1.27	3	160 (5)	89.0	92.0	7.7	33.9	110.0*	121.0	8.5	34.3
C	4.13	1.27	3	143 (16)	86.0	91.1	10.3	38.7	109.3	113.2	12.4	40.4
D	4.38	1.04	3	143 (18)	88.0	95.2	14.1	44.7	107.0	115.6	12.7	44.2
D	4.38	1.04	6	143 (11)	93.0	96.2	10.8	34.4	112.0	118.0	12.2	40.7
D	4.38	1.04	6	143 (16)	98.5	99.0	9.0	35.0	112.0	118.0	12.2	34.2
E	5.70	1.29	3	160 (16)	95.2	98.3	6.0	16.9	114.0	123.0	4.0	16.6
E	5.70	1.29	3	160 (6)	94.2	98.6	7.9	25.4	111.0	123.0	7.5	23.0
F	4.01	0.84	6	143 (30)	88.1	90.8	10.5	39.4	104.8	111.2	11.2	47.1
F	4.01	0.84	6	143 (24)	85.0	88.2	13.0	39.7				51.0
G	6.00	1.00	3	160 (16)	103.0	105.0	3.8	18.7	123.0	128.0	3.6	19.2
G	6.00	1.00	3	160 (6)	87.6	92.8	8.0	30.0	113.0	121.0	6.5	32.6
H	4.23	0.73	6	143 (35)	88.9	91.2	9.6	45.7	106.1	113.4	11.1	47.4
I	4.28	0.85	6	143 (14)	88.4	92.4	11.2	42.8	108.3	115.3	11.5	45.4
J	3.95	1.03	6	143 (13)	88.9	92.0	10.5	40.8	104.5	112.0	9.2	43.1
K	4.19	1.21	6	143 (12)	81.1	89.2	11.2	41.2	99.7	110.0	11.8	40.0
K	4.19	1.21	6	127 (100)	88.4	94.7	8.8	36.6	103.4	113.4	10.9	36.4
K	4.19	1.21	6	143 (22)	90.7	94.9	10.1	31.9	108.7	116.0	9.4	31.0
K	4.19	1.21	6	160 (4.5)	91.0	94.4	7.8	28.4	108.6	115.5	8.7	28.8
L	4.00	1.41	6	143 (16)	88.5	91.1	5.6	24.8	106.2	112.0	8.5	24.3
M	3.78	1.81	6	143 (24)	91.4	93.0	6.2	16.0	111.0	115.1	3.9	15.7
N	4.04	0.86	6	143 (14)	81.5	88.0	10.3					
N	4.04	0.86	6	143 (20)	85.5	89.9	10.3	36.9	103.5	111.8	11.7	46.9
N	4.04	0.86	6	143 (22)	90.0	92.8	9.5	35.8	105.3	112.6	9.9	42.5
O	4.28	0.84	6	143 (14)	87.8	92.2	12.0	44.6	96.8	111.0	13.2	47.0
O	4.28	0.84	6	143 (24)	94.9	96.8	10.2	33.2	115.0	121.2	8.9	37.1
P	4.31	0.80	6	143 (14)	89.6	93.9	11.6	42.2	105.0	113.0	12.2	47.5
P	4.31	0.80	6	143 (18)	91.2	94.5	11.3	39.1	111.5	117.0	9.4	47.6
Q	4.04	0.85	6	143 (20)	86.0	90.5	10.7	45.7	110.0	118.1	10.5	47.3
Q	4.04	0.85	6	143 (24)	90.8	93.2	9.1	43.6	111.0	117.8	11.2	48.0
Q	4.04	0.85	6	143 (34)	93.8	95.0	9.6	39.2	113.5	118.5	8.7	39.3
R	4.90	1.15	0	170 (15)	87.0	93.9	6.8	26.1	105.0	112.5	4.1	21.1
R	4.90	1.15	1.5	160 (10)	88.1	95.5	9.4	28.9	106.0	115.1	8.3	25.4
R	4.90	1.15	4	160 (13)	89.2	95.3	11.1	33.2	114.5	120.0	10.8	32.7
R	4.90	1.15	7	143 (9)	88.2	94.0	12.0	32.7	106.2	114.8	12.7	34.6
R	4.90	1.15	9.5	143 (9)	88.1	94.2	10.9	34.8	113.0	118.5	8.5	36.7
S	3.58	0.93	6	143 (20)	91.2	94.2	12.4	38.9	112.1	118.9	5.2	43.6
T	3.79	0.92	6	143 (28)	94.0	95.8	9.9	35.9	114.0	119.8	9.4	36.1
V	3.62	0.99	6	143 (26)	90.0	91.5	8.7	38.7	114.8	120.0	9.6	40.7
W	3.61	0.91	6	143 (28)	90.5	92.5	9.8	38.5	108.0	115.2	11.3	38.2
W	3.61	0.91	6	143 (44)	89.0	90.1	7.8	36.4	112.8	118.5	10.9	31.8
X	2.8	0.86	6	143 (12)	55.9	68.8	18.9					
X	2.8	0.86	6	143 (30)	74.3	78.3	12.3					
X	2.8	0.86	6	143 (60)	78.6	81.7	11.8					
X	2.8	0.86	6	143 (90)	82.2	84.9	12.0	50.0				
Y	3.5	0.79	6	143 (12)	71.2	79.0	14.3					
Y	3.5	0.79	6	143 (30)	84.3	88.0	13.3					
Y	3.5	0.79	6	143 (60)	86.3	88.9	12.3	50.0				
Y	3.5	0.79	6	143 (75)	87.3	89.9	11.2					
Y	3.5	0.79	6	143 (90)	88.7	90.0	11.1					

TABLE 3-continued

Properties For Varying Compositions With Varying Stretch And Artificial Aging

					Room temperature				−196° C.			
Alloy (wt. %)	Cu (wt. %)	Li (wt. %)	Stretch	Aging (°C. (h))	YS (ksi)	UTS (ksi)	El. (%)	K_{IC} (ksi√in)	YS (ksi)	UTS (ksi)	El. (%)	K_{IC} (ksi√in)
Z	2.16	0.80	6	143 (30)	47.2	60.0	21.2					
Z	2.16	0.80	6	143 (100)	64.9	69.0	13.8					
AA	3.18	0.78	6	143 (60)	63.0	70.8	17.2					
AA	3.18	0.78	6	143 (90)	78.3	81.1	13.0					
AA	3.18	0.78	6	143 (100)	78.5	81.2	12.8	50.0				
BB	3.56	0.29	6	143 (60)	63.0	70.8	17.2					
BB	3.56	0.29	6	143 (100)	67.5	72.0	14.2					
CC	3.43	0.56	6	143 (60)	70.6	77.0	12.8					
CC	3.43	0.56	6	143 (90)	76.0	79.3	12.8					
CC	3.43	0.56	6	143 (100)	76.7	80.0	11.5					
DD	3.41	1.12	3	143 (24)	88.5	91.8	7.9	29.8	108.4	116.0	10.9	42.0
DD	3.41	1.12	6	143 (16)	88.4	90.8	8.9	28.7	107.2	114.5	11.3	42.1
DD	3.41	1.12	6	143 (60)	95.5	96.8	6.4	25.2	116.2	121.5	9.0	33.0
EE (long).	4.47	0.95	3	160 (6)	86.5	90.9	10.4	40.7	106.2	114.5	11.2	49.3
EE (LT)	4.47	0.95	3	160 (6)	70.5	78.0	8.4	30.8	74.2	95.5	10.5	36.4

*estimated from other data

COMPOSITION

In accordance with the present invention, the desirable cryogenic fracture toughness trend can be achieved by controlling Cu and Li levels. Copper levels of from about 3.0 to about 4.5% and lithium levels of from about 0.7 to about 1.1% are most preferred in order to most readily attain the desirable trend at high strength levels. However, the desirable trend can be achieved for copper levels of from about 2.0 to about 6.5% and lithium levels of from about 0.2 to about 2.7%. In order to produce the desirable cryogenic fracture toughness trend while at the same time producing high levels of strength, Cu levels of 2.8 to 4.8% and Li levels of 0.4 to 1.5% are more preferred. Within these compositional ranges, the combined cryogenic fracture toughness and strength properties are maximized, making such alloys highly superior for cryogenic use. One particularly preferred alloy for cryogenic use comprises 4.0% Cu and 1.0% Li, while another highly preferred alloy comprises 4.5% Cu and 0.8% Li. The amounts of Cu and Li employed are interdependent. For example, for copper levels at the high end of the broad range, e.g., 6.5%, the level of lithium should be close to about 1.0% to achieve the desirable cryogenic fracture toughness trend at high strength levels. At the lower end of the broad Cu range, e.g., 2.0%, more Li can be present but the highest strength attainable will generally be lower, as shown by Alloy Z (see Table 3). Conversely, when the level of lithium is at the low end of the broad range, e.g., 0.2%, the level of copper can be relatively high and the desirable trend can be achieved, but strength will be lower than at higher Li levels of about 1% shown by Alloy BB (see Table 3). At the high end of the broad Li range, e g , 2.7% lower Cu levels such as 2% are preferred in order to attain the desirable trend.

Copper and lithium levels have a significant effect on the strength levels attained in the present alloys. Copper levels above about 4% produce the highest strengths, with significant decreases in strength below about 3% (see Alloy Z in Table 3). In addition, the highest strengths are attained with Li levels of from about 1.05 to about 1.35%, with a peak at about 1.2% lithium. Significant decreases in strength result below about 0.5% and above about 1.5% Li (see Alloy BB in comparison to Alloy CC in Table 3). Thus, while the desirable cryogenic fracture toughness trend is most easily attained and strength levels are very high at copper levels of about 4% and lithium levels of about 1%, lowering of the copper and lithium levels significantly below these amounts may still result in the desirable trend, but with lower strengths. The alloys of the present invention comprising from about 2.8 to about 4.8 percent Cu and from about 0.4 to about 1.5 percent Li have been found to possess superior combinations of both cryogenic fracture toughness and strength properties, thus providing for surprisingly increased performance when used at cryogenic temperatures. The high toughnesses are obtained without the delamination associated with alloys such as 2090, which has inflated toughness values due to an effect known as "delamination toughening". Consequently, alloys such as 2090 actually display lower fracture strength than 2219 in actual tank gages.

The amount of copper and lithium used also affects the processing that must be employed to achieve the desired trend. For example, at the most preferred levels of about 4.0% copper and 1.0% lithium, little or no stretch may be required to achieve the desired trend at high strength levels. However, as the boundaries of the copper and lithium ranges are reached, optimal amounts of stretch and carefully controlled artificial aging treatments may be required in order to produce the desired cryogenic fracture toughness trend at technologically useful strength levels.

The amount of magnesium used in the present alloys has only a minor effect on the cryogenic fracture toughness trend. However, the strength of the alloys is highly dependent on Mg content, with peak strengths being attained at Mg levels of from about 0.3 to about 0.6 percent. Furthermore, increasing the Mg content to levels of about 0.6 to about 1.0% increases the absolute toughness values at the preferred Cu and Li levels.

The presence or absence of silver in the alloys of the present invention does not significantly affect the cryogenic fracture toughness trend. However, Ag produces an improvement in strength.

While the amount of zinc used in the alloys does not appear to have a significant effect on the cryogenic fracture toughness trend, strength levels and aging kinetics (the rate at which the alloys progress along the aging curve) may be increased with the addition of minor amounts of Zn (see Alloys S, T, W, X and Y in Table 3). Thus, additions of Zn and/or Ag do not adversely affect the ability to attain the desirable toughness trend, but their presence may be advantageous for improving other properties such as strength.

STRETCH

The amount of stretch employed in accordance with the present invention has a significant effect on cryogenic fracture toughness and the ability to attain the desirable trend. In general, greater amounts of stretch result in an improved cryogenic fracture toughness trend. For a given Al—Cu—Li alloy, a crossover point may be demonstrated, wherein the desirable trend is achieved above a certain stretch level but is not achieved below that level. FIG. 5 shows one such crossover point. In the alloy illustrated in FIG. 5, the crossover occurs at between 4 and 5% stretch at the 90 ksi strength level. However, this point may change as composition and processing variables are altered. For compositions near the 4.0 Cu and 1.0 Li levels, the amount of stretch may not be as critical. However, near the upper boundaries of the broad Cu and Li ranges as shown in Table 1, the provision of a significant amount of stretch may be necessary in order to attain the desirable cryogenic fracture toughness trend. The amount of stretch employed is also dependent upon the degree of artificial aging used, as more fully described below.

ARTIFICIAL AGING

In accordance with the present invention, artificial aging has a significant effect on the cryogenic fracture toughness trend. In general, underaging tends to produce the desirable trend in comparison to peak or over aging. By aging to a point below peak strength, the desirable trend is more readily attained. For example, while a given alloy of the present invention may be capable of attaining a peak yield strength of 100 ksi, underaging to a yield strength of 90 ksi is more likely to produce the desired cryogenic fracture toughness trend. This phenomena is not fully understood, but a possible explanation may involve the transition from intersubgranular to microvoid fracture. The degree of underaging required is dependent upon alloy composition and processing history. For example, at a preferred copper level of 4% and lithium level of 1%, or 4.5% copper and 0.8% lithium, for a technologically wide range of stretch levels, underaging may not be required and the desirable trend can be achieved at peak strength. However, near the upper copper and lithium boundaries, significant underaging may be required in order to produce the desired trend. A typical underaging treatment is to artificially age the alloy to a yield strength that is at least about 5 ksi below the peak yield strength of the alloy. Such underaging has been found to significantly promote the desirable cryogenic fracture toughness trend. To attain the desirable trend with greater safety margin in a production environment, it may be preferable to age to a yield strength that is about 10 to 20 ksi below the peak yield strength. It is significant that the alloys of the present invention can attain such high peak strengths because technologically useful strengths can still be achieved with significant underaging.

RECRYSTALLIZATION

For wrought Al—Cu—Li alloys in plate, sheet, extrusion, forging and other forms, the cryogenic fracture toughness trend can be significantly affected by the amount of recrystallization. In general, unrecrystallized plate tends to promote the desired cryogenic toughness trend while recrystallized plate tends to decrease the ease with which the desired trend can be attained after solution heat treatment, stretching and aging. Furthermore, the unrecrystallized microstructure is desirable for increased fracture toughness at a given temperature. It may therefore be desirable to, for example, roll the alloy at higher temperatures at which recrystallization is less likely to occur than at lower temperatures at which recrystallization may be induced. For products with higher amounts of recrystallization, a greater degree of underaging and/or a greater amount of stretch is generally necessary to attain the desirable cryogenic toughness trend. Furthermore, lowering the amount of Cu and/or Li may enable greater amounts of recrystallization to be tolerated while still achieving the desirable trend after subsequent solution heat treatment, quenching, stretching and artificial aging.

FABRICATION OF CRYOGENIC CONTAINER

Alloys of the present invention may be rolled, extruded and forged to the product forms necessary to fabricate a container for holding cryogenic materials. Such a cryogenic tank, when used for holding cryogenic liquids such as liquid hydrogen, oxygen or nitrogen, generally consists of the barrel, which is a hollow cylinder, the domes, which are approximately hemispherical in shape, and the rings, which connect the barrel to the fore and aft domes. The barrel may be fabricated from plate that has been processed in accordance with the present invention and which is subsequently machined so that it has longitudinal T-shaped or L-shaped stiffeners. Alternatively, the barrel may be fabricated from integrally-stiffened extrusions which have the T-shaped or L-shaped longitudinal stiffeners introduced during the extrusion event. Furthermore, simple stiffeners may be rolled into the plate, e.g., linear stiffeners. The ring can be formed from extrusions that are bent over a curved tool and welded into a ring, or roll-ring forged, an operation in which a billet is pierced to a doughnut shape and the wall thickness is worked to thinner gages as the diameter increases. The domes may be formed from gore panels of plate or sheet that are stretched over a tool and welded together. Alternatively, the dome can be spin-formed from plate at cold, warm, or hot working temperatures.

In each of these components of the cryogenic tank, the amount of stretch necessary to produce the desirable cryogenic toughness trend can be introduced during the forming operation after solution heat treatment and quench. For example, the plate and extrusion can be simply stretch straightened. Alternatively, cold work can be introduced when the gore panels are stretched over a mandrel, the barrel panels are bump formed over a tool, the ring extrusions are bent and stretched over a tool to introduce curvature, or the dome is spun formed. The artificial aging conditions are selected as previously disclosed to ensure that the desirable trend is achieved.

The tank components may be welded together by virtually any of the conventional welding techniques, including gas tungsten arc welding, dual torch gas tungsten arc welding, metal inert gas welding, variable polarity plasma arc welding, variable polarity gas tungsten arc welding, electron beam welding and others. Conventional filler alloys such as 2319 are acceptable, as are parent filler alloys of the present invention. In addition, parent alloys containing greater amounts of grain refiners, e.g., Zr and Ti, and slightly greater Cu content are often preferred to increase weldment strength.

In fabricating the cryogenic tank or container, the barrel panels are welded together forming a right circular cylinder which is then welded to the ring. The two domes are each welded to a ring, thereby forming the cryogenic tank. It is noted that the cryogenic tank typically also has secondary hardware that may be fabricated by forging to asymmetric shapes, i.e., that cannot be stretched. These components should contain the more preferred amounts of Cu and Li, e.g., 2.8–4.8 Cu and 0.7–1.1 Li, to enable the desirable trend to be attained with no stretch, while still maintaining high strength levels. For some forgings, cold work could be practically introduced by shot peening.

The components of the cryogenic tank can be welded by various parameters depending upon the technique selected. A preferred route is to weld the components using conventional gas tungsten arc welding with conventional 2319 filler. The surfaces to be welded should preferably be mechanically milled or chemically milled in a 100 g/l NaOH aqueous solution such that about 0.5 mm of the surface is removed. A 75% Ar/25% He inert gas cover at 14 /min can be used. For 1 mm diameter 2319 filler, a travel speed of 25 cm/min at a current of 170 Amps and a voltage of 12.5 volts produces high integrity weldments. If the weight of the tank needs to be decreased, conventional chemical milling could be used to reduce the thickness of the barrel in low service load areas. A typical solution for such milling is 103 g/l NaOH, 22 g/l sodium sulphide and 2.2 g/l sodium gluconate to make 1 liter of solution.

Weldments made as described above also display increasing weldment toughness and strength with decreasing temperature. The tank so fabricated can be cost effectively proof tested at room temperature. Because toughness and strength are each substantially the same or greater at cryogenic service temperatures than at the ambient proof test temperature, the tank can be safely used with minimal risk of toughness-limited or strength-overload-induced failures.

It is to be understood that the above description of the present invention is susceptible to various modifications, changes and adaptations by those skilled in the art and that such modifications, changes and adaptations are to be considered to be within the spirit and scope of the invention as set forth by the claims which follow.

What is claimed is:

1. A method for producing an improved aluminum-base alloy comprising the steps of:

a) providing a solution heat treated and quenched aluminum-base alloy consisting essentially of from 2.0 to 6.5 weight percent Cu, from 0.2 to 2.0 weight percent Li, and the balance aluminum and incidental impurities; and

b) at least one of working and artificially aging said alloy in an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature, wherein the fracture toughness at room temperature is at least 18.7 ksi√in and the fracture toughness at −196° C. is at least 19.2 ksi√in.

2. A method according to claim 1, wherein said aluminum-base alloy further contains Mg in an amount up to 40. weight percent and from 0.01 to 1.0 weight percent of at least one grain refiner selected from the group consisting of Zr, Ti, Cr, Mn, Hf, Nb, B, V, and TiB_2.

3. A method according to claim 1, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 4.0 weight percent, Mg in an amount up to 4.0 weight percent, and Zn in an amount up to 3.0 weight percent.

4. A method according to claim 2, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 4.0 weight percent, Mg in an amount up to 4.0 weight percent, and Zn in an amount up to 3.0 weight percent.

5. A method according to claim 1, wherein said working of said alloy is performed substantially at room temperature.

6. A method according to claim 1, wherein said working of said alloy is achieved by introducing the equivalent of from 3 to 7 percent stretch to said alloy.

7. A method according to claim 1, wherein the time and temperature at which said artificial aging is performed results in underaging of said alloy to a yield strength at least 5 ksi below the peak yield strength that said alloy is capable of attaining.

8. A method according to claim 1, wherein said artificial aging is performed at a temperature of from 125° to 150° C.

9. A method according to claim 1, wherein said Cu comprises from 2.8 to 4.8 weight percent, said Li comprises from 0.4 to 1.5 weight percent, and furthermore comprises Mg in an amount from 0.2 to 1.0 weight percent of said alloy.

10. A method according to claim 2, wherein said Cu comprises from 2.8 to 4.8 weight percent, said Li comprises from 0.4 to 1.5 weight percent, and the aluminum base alloy furthermore comprises Mg in an amount from 0.2 to 1.0 weight percent of said alloy.

11. A method according to claim 9, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount up to 1.0 weight percent.

12. A method according to claim 10, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount up to 1.0 weight percent.

13. A method according to claim 4, wherein said Cu comprises from 3.0 to 4.5 weight percent, said Li comprises from 0.7 to 1.1 weight percent, said Mg comprises from 0.3 to 0.6 weight percent, and said grain refiner comprises from 0.08 to 0.3 weight percent of said alloy, wherein said grain refiner is selected from the group consisting of Zr, Ti, and combinations thereof.

14. A method according to claim 2, wherein said Cu comprises from 2.8 to 4.8 weight percent, said Li comprises from 0.4 to 1.5 weight percent, and the aluminum base alloy furthermore comprises Mg in an amount from 0.2 to 1.0 weight percent of said alloy.

15. A method according to claim 14, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount up to 1.0 weight percent.

16. A method according to claim 13, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount up to 1.0 weight percent.

17. A method according to claim 1, wherein the yield strength of said alloy at cryogenic temperature is greater than its yield strength at room temperature, which is greater than 85 ksi (longitudinal), and the plane strain fracture toughness of said alloy at cryogenic temperature is greater than its plane strain fracture toughness at room temperature, which is greater than 25 ksi√in.

18. A method according to claim 13, wherein the yield strength of said alloy at cryogenic temperature is greater than its yield strength at room temperature, which is greater

than 85 ksi (longitudinal), and the plane strain fracture toughness of said alloy at cryogenic temperature is greater than its plane strain fracture toughness at room temperature, which is greater than 25 ksi√in.

19. A wrought aluminum-base alloy consisting essentially of from 2.8 to 4.8 weight percent Cu, from 0.4 to 1.5 weight percent Li, from 0.2 to 1.0 weigth percent Mg, and the balance aluminum and incidental impurities, wherein said alloy is worked, artificially aged, or worked and artificially aged an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature, wherein the fracture toughness at room temperature is a least 18.7 ksi√in.

20. A wrought aluminum-base alloy according to claim **19**, wherein said alloy further contains from 0.01 to 1.0 weight percent of at least one grain refiner selected from the group consisting of Zr, Ti, Cr, Mn, Hf, Nb, B, V, and TiB_2.

21. A wrought aluminum-base alloy according to claim **20**, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount of up to 1.0 weight percent.

22. A wrought aluminum-base alloy according to claim **20**, wherein said Cu comprises from 3.0 to 4.5 weight percent, said Li comprises from 0.7 to 1.1 weight percent, said Mg comprises from about 0.3 to about 0.6 weight percent, and said grain refiner comprises from 0.08 to 0.3 weight percent of said alloy, wherein said grain refiner is selected from the group consisting of Zr, Ti and combinations thereof.

23. A wrought aluminum-base alloy according to claim **21**, wherein said Cu comprises from 3.0 to 4.5 weight percent, said Li comprises from 0.7 to 1.1 weight percent, said Mg comprises from about 0.3 to about 0.6 weight percent, and said grain refiner comprises from 0.08 to 0.3 weight percent of said alloy, wherein said grain refiner is selected from the group consisting of Zr, Ti, and combinations thereof.

24. A wrought aluminum-base alloy according to claim **20**, wherein said Cu comprises from about 3.0 to about 4.5 weight percent of said alloy.

25. A wrought aluminum-base alloy according to claim **20**, wherein said Li comprises from about 0.7 to about 1.1 weight percent of said alloy.

26. A wrought aluminum-base alloy according to claim **20**, wherein said alloy is in the form of an extrusion.

27. A wrought aluminum-base alloy according to claim **20**, wherein said alloy is in the form of a plate.

28. A wrought aluminum-base alloy according to claim **20**, wherein said alloy is in the form of a sheet.

29. A wrought aluminum-base alloy according to claim **20**, wherein the yield strength of said alloy at cryogenic temperature is substantially equal to greater than its yield strength at room temperature, which is greater than 85 ksi, and the plane strain fracture toughness of said alloy at cryogenic temperature is greater than its plane strain fracture toughness at room temperature, which is greater than 25 ksi√in.

30. A wrought aluminum-base alloy according to claim **20**, wherein the yield strength of said alloy at cryogenic temperature is greater than its yield strength at room temperature, which is greater than 85 ksi, and the plane stress fracture toughness of said alloy at cryogenic temperature is greater than its plane stress fracture toughness at room temperature, which is greater than 25 ksi√in.

31. A wrought aluminum-base alloy according to claim **20**, wherein said alloy is underaged to a yield strength at least 5 ksi below the peak yield strength that said alloy is capable of attaining.

32. A cryogenic material-holding container made from an alloy consisting essentially of from 2.8 to 4.5 weight percent Cu, from 0.4 to 1.5 weight percent Li, from 0.2 to 1.0 weight percent Mg, and the balance aluminum and incidental impurities, wherein said alloy is worked, artificially aged, or worked and artificially aged an amount sufficient to provide strength and fracture toughness to said alloy at cryogenic temperature substantially equal to or greater than the strength and fracture toughness at room temperature, wherein the fracture toughness at room temperature is at least 18.7 ksi√in and the fracture toughness at −196° C. is at least 19.2 ksi√in.

33. A cryogenic material-holding container according to claim **32**, wherein said alloy further contains from 0.01 to 1.0 weight percent of at least one grain refiner selected from the group consisting of Zr, Ti, Cr, Mn, Hf, Nb, B, V, and TiB_2.

34. A cryogenic material-holding container according to claim **33**, wherein said aluminum-base alloy further contains at least one of Ag in an amount up to 0.8 weight percent and Zn in an amount of up to 1.0 weight percent.

35. A cryogenic material-holding container according to claim **33**, wherein the yield strength of said alloy at cryogenic temperature is greater than its yield strength at room temperature, which is greater than 85 ksi (longitudinal), and the plane strain fracture toughness of said alloy at cryogenic temperature is greater than its plane strain fracture toughness at room temperature, which is greater than 25 ksi√in.

36. A cryogenic material-holding container according to claim **33**, wherein the yield strength of said alloy at cryogenic temperature is greater than its yield strength at room temperature, which is greater than 85 ksi (longitudinal), and the plane stress fracture toughness of said alloy at cryogenic temperature is greater than its plane stress fracture toughness at room temperature, which is greater than 25 ksi√in.

37. A cryogenic material-holding container according to claim **33**, wherein said alloy is underaged to a yield strength at least about 5 ksi below the peak yield strength that said alloy is capable of attaining.

38. A cryogenic material-holding container according to claim **33**, wherein said container has been formed by welding.

39. A cryogenic material-holding container according to claim **33**, wherein said cryogenic material is selected from the group consisting of liquid hydrogen, liquid oxygen, and liquid nitrogen.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,455,003 Page 1 of 2
DATED : October 3, 1995
INVENTOR(S) : Joseph R. Pickens et al

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 2, line 12, "1.9-2.6)" should read --(1.9-2.6)--; line 38, delete the extra spaces between "max." and "Zn".

Column 7, line 57, after "C." (first occurrence) insert a comma (,); line 61, after "C." (first occurrence) insert a comma (,); line 64, after "C." insert a comma (,).

Column 8, line 24, "(16 h" should read --(16h--; line 35, after "C." insert a comma (,); line 46, "Ys" should read --YS--; line 57, "1 h" should read --1h--; line 67, "EXAMPLE 6" should be centered in column.

Column 9, line 15, "EXAMPLE 7" should be centered in column; line 30, "EXAMPLE 8" should be centered in column; line 41, after "C." insert a comma (,); line 46 "EXAMPLE 9" should be centered in column.

Column 10, line 3, after "C." insert a comma (,); line 59, after "C." insert a comma (,); line 66, after "C." insert a comma (,). (2nd Occur.

Column 12, line 46, "94 4" should read --94.4--; line 47, "28 4" should read --28.4--.

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 5,455,003 Page 2 of 2

DATED : October 3, 1995

INVENTOR(S) : Joseph R. Pickens et al

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Column 14, line 34, "1 12%" should read --1.12%--; line 38, after "III)" insert a period (.); line 53, after "III)" insert a period (.); line 58, delete the extra spaces between "composition" and "Al".

Column 17, line 55, after "1%" insert a comma --, as--; line 56, "e g , 2.7%" should read --e.g., 2.7%,".

Column 21, lines 20 and 21, "14/min" should read --14 l/min--; line 61, "40" should read --4.0--.

Column 23, line 14, before the period (.) add --and the fracture toughness at -196°C is at least 19.2 ksi$\sqrt{in}$--.

Signed and Sealed this

Fifth Day of March, 1996

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks

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